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Concord, MA

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Total, inhalable and fine particulate matter measurements acquired by EPA's Inhalable Particulate Network in 1979 and 1980 are summarized and analyzed in this report. The theoretical collection efficiencies of different samplers were calculated and compared to each other and to an acceptable performance range. The measurement processes and several of the major urban airsheds of the IP Network are described. The spatial, temporal and statistical distributions of these measurements are examined. A receptor-oriented model relating IP to TSP is derived and tested for prediction accuracy under various situations. A mass balance receptor model is applied to IP and FP chemical concentrations in four urban areas to estimate the contributions of various emissions source types to ambient mass concentrations.

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Analysis of Inhalable and Fine Particulate Matter Measurements

by

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise and Radiation
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ABSTRACT

Total, inhalable and fine particulate matter measurements acquired by EPA's Inhalable Particulate Network in 1979 and 1980 are summarized and analyzed in this report. The theoretical collection efficiencies of different samplers were calculated and compared to each other and to an acceptable performance range. The measurement processes and several of the major urban airsheds of the IP Network are described. The spatial, temporal and statistical distributions of these measurements are examined. A receptor-oriented model relating IP to TSP is derived and tested for prediction accuracy under various situations. A mass balance receptor model is applied to IP and FP chemical concentrations in four urban areas to estimate the contributions of various emissions source types to ambient mass concentrations.

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J.G.W.
J.C.C.
J.J.S.

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EXECUTIVE SUMMARY

The advent of a new size-specific standard for suspended particulate matter mass concentrations has motivated measurement programs to quantify the concentrations of fine (that portion of ambient aerosol consisting of particles with aerodynamic diameters less than approximately 2.5 um) and inhalable (the portion consisting of particles of aerodynamic diameters less than 15 um) particulate matter in urban and non-urban parts of the United States. The United States Environmental Protection Agency (EPA)'s Inhalable Particulate Network is the most comprehensive of these monitoring programs. Recently, it has been recommended that a size-specific standard based on the fraction of ambient aerosol with particle sizes less than approximately 10 um in aerodynamic diameter be considered, but no such measurements are yet available.

The data from the EPA and other networks are interpreted in this report and the extent to which they might apply to a 10 um standard is evaluated. The topics which are addressed and the major conclusions derived from them are presented in this executive summary.

Aerosol Sampler Collection Characterisitcs

The products of typical aerosol size distributions and collection effectiveness curves of IP Network and other samplers, resulting from wind tunnel study tests, were integrated over particle size to calculate absolute collection efficiencies. The efficiencies of different samplers were compared to each other and to an acceptable performance range. Though dichotomous sampler collection effectiveness curves do not fall within the acceptable performance range, the collection efficiency does meet the collection efficiency requirements of that range under typical wind speeds and particle size distributions. HIVOL samplers with size-selective inlets satisfy both collection effectiveness and collection efficiency requirements. The efficiencies of samplers which would fall within EPA's proposed acceptable performance window range from 47 to 71% for a typical urban size distribution. A sampler with an effectiveness curve designed to meet the lower limit would sample 66% of the mass of a sampler designed to correspond to the upper limit. Inlets with 10 um 50% cut-sizes can be expected to collect between 80 and 90% of the mass collected with the present dichotomous and HIVOL size-selective inlets. HIVOL samplers with size-selective inlets and dichotomous samplers should sample equivalent mass concentrations within 5% of each other under typical situations. However, under low or high wind speeds, in particle size distributions with much coarse material, or when interferences are present in one or both of the samplers, this equivalency degrades. Results of the collection efficiency model agree with average ratios determined from ambient measurements. These average ratios show substantial variability due to insufficient knowledge of the ambient particle size distribution and wind speed during ambient sampling.

The Inhalable Particulate Network Measurement Process

The IP Network made mass, ion and elemental concentration measurements of total (TSP), inhalable (IP) and fine (FP) suspended particulate matter at urban and non-urban sampling sites throughout the United States. The interpretation of these data cannot be separated from the measurement process.

The study scale is urban-scale with some regional-scale and neighborhood-scale sites. Most sampling site locations seem to be representative of the study scales for which they were selected.

A change in the fibrous filter media for high-volume sampling after the beginning of 1980 could result in differences between sulfate, nitrate and mass measurements that are products of the measurement process rather than an environmental cause.

The data validation procedure to which IP Network mass data are submitted identifies many internal inconsistencies as well as extreme cases; the total number of these cases amounts to a large portion of the data base. For the purposes of this report, several of these flagged values were deleted. Data validation procedures have been applied only to mass measurements; (no validation flags appear on reports of chemical composition) and should be extended to ion and element measurements.

Tests on high-volume samplers show that coppper emissions from the motor can interfere with copper measurements from nearby samplers and that deposition on the filter during standby periods can interfere with mass measurements.

The comparison of collocated high-volume sampler measurements in the IP Network is similar to comparisons in other networks showing average differences between simultaneous samples of less than 5% of the average mass concentration. Collocated dichotomous samplers have been shown to attain average differences of less than 10% of the average IP mass concentration.

Urban Areas in the Inhalable Particulate Network

The urban areas sampled by the IP Network represent a broad coverage of population, meteorological, and emissions cases. Though not all urban areas in the United States are represented, the ones that were chosen include major population centers with varying population densities. Major particulate matter sources have been identified and located on maps with respect to IP Network sampling sites in Birmingham, AL, Phoenix, AZ, Denver, CO, Buffalo, NY, Philadelphia, PA, Houston, TX and El Paso, TX.

Several of the sites in the IP Network were found to be in proximity to industrial sources which emit chemical species measured on IP Network samples. These concentrations can be used to quantify source contributions to receptors.

Geographical and Seasonal Variability of IP and FP in Urban Areas

Annual arithmetic averages of IP and FP can exceed 90 ug/m^3 and 35 ug/m^3, respectively, in urban areas, though the typical average concentrations appear to be approximately 50 ug/m^3 and 25 ug/m^3, respectively. Primary standards for annual IP averages in the 55 to 120 ug/m^3 range (Hileman, 1981) would find most, and possibly all, of the sites examined in compliance. This range is tentative and may have been modified subsequent to the writing of this report.

Annual 24-hr maximum concentrations of IP and FP can exceed 200 ug/m^3 and 100 ug/m^3, respectively, in urban areas. Typical values are approximately 100 ug/m^3 for IP and 60 ug/m^3 for FP. Hileman (1981) cites a 24-hr maximum IP range of 150 to 350 ug/m^3 for a primary standard and a 24-hr maximum FP range of 70 to 220 ug/m^3 for a secondary standard. Once again, most, if not all IP Network sites would be in compliance with such a standard. The values cited by Hileman (1981) are tentative and the form and values of a 24-hr standard may have been modified subsequent to the writing of this report.

The urban and neighborhood-scale IP and FP measurements vary significantly from site to site within the areas studied. The implications are that (1) local (within a few kilometers of the sampler) sources are significant contributors to IP concentrations and (2) present spacing between sampling sites may be inadequate to fully represent IP concentrations in certain urban areas and neighborhoods.

Seasonal averages of IP and FP tend to peak slightly in the summer periods, but there are many individual exceptions at IP Network sites. This conclusion is speculative because of the inadequate seasonal data available for this report. If the conclusion is valid, then sampling should take place on a yearly basis for the determination of long-term averages so that all seasons are equally weighted. A seasonally-weighted annual average might be a more appropriate method of calculating the annual average if the number of samples in one or more seasons differs by a large amount from the number of samples taken in another season.

Geographical and Seasonal Variability of IP and FP in Non-Urban Areas

Non-urban average IP and FP concentrations are nominally 30 and 10 ug/m^3, respectively, in the western United States and 30 and 20 ug/m^3, respectively, in the eastern United States. The number of non-urban sites with sufficient data in the West is small, however, and these observations should carry less weight than those from the East where independent measurements corroborate each other.

There is a general seasonal variability of average IP and FP concentrations in the eastern United States in which the spring and summer month concentrations are elevated with respect to the fall and winter months. Independent measurements from different networks support this conclusion. Though the measurements in the western United States do not show significant deviations between seasons, the number of sites examined is too small to allow a general conclusion.

Up to 60% of the IP and 70% of the FP in urban areas can typically be accounted for by concentrations present at nearby non-urban sites. This portion varies substantially from site to site and is based on a limited number of sites, primarily in the eastern United States. Much of the non-urban concentrations may have originated from far away anthropogenic sources.

Statistics of IP and FP Concentrations

One percent of the IP Network measurements exceeded 170 ug/m^3 for the high-volume size-selective inlet samples (SSI), 150 ug/m^3 for the dichotomous IP samples (TOTAL), 80 ug/m^3 for FP and 90 ug/m^3 for coarse particulate matter (CP) samples.

The cumulative frequency distributions at individual sites show examples of the TSP patterns advanced by deNevers et al (1979) as well as approximations to log-normal distributions. The small number of measurements available at most sites prevents an assessment of the adequacy of the log-normal and other statistical distributions in representing IP and FP data.

The geometric and arithmetic averages of IP and FP data sets normally differ by 5 to 15% with respect to the arithmetic average, though the difference is as large as 37% for IP Network data. The ratios of geometric to arithmetic averages which are calculated from different subsets of all possible measurements at a site are constant to within ±5% until the number of measurements in the subset falls below five.

Arithmetic averages of IP and FP tend to remain constant, within ±10%, as the number of days between samples is increased. For 15 or fewer samples this consistency breaks down.

Maximum concentrations of IP and FP are extremely sensitive to sample size and can be reduced by 50% as the number of days separating samples is increased. This means that any standard, such as the present one, which specifies a maximum concentration, should also specify a sampling frequency, or that other forms of short-term standards should be considered.

Predicting IP Concentrations from TSP Concentrations

The average ratio of IP to TSP derived from a number of different data sets was used to predict IP concentrations from TSP concentrations under a variety of conditions. The predicted values were compared with measurements taken simultaneously with the TSP measurements used in the model.

No simple relationship between FP and TSP was found which would predict FP from TSP with adequate precision. For IP Network data nearly 70% of the FP predictions differed from the measurements by more than ±20%.

The average ratio model derived from all IP Network measurements is the simplest relationship between IP and TSP. For size-selective inlet and dichotomous sampler IP measurements, stratification by site type does not increase the precision of the model's predictions. The model is independent of TSP concentrations for size-selective inlet predictions, but it exhibits a TSP concentration dependency for TOTAL predictions. Seventy-six percent of the size-selective inlet measurements and 57% of the dichotomous sampler IP measurements were predicted to within ±20% by this model in the IP Network.

Models derived from simultaneous TSP and IP sampling at a single site in an industrial neighborhood predicted IP concentrations from TSP concentations at nearby sites in the neighborhood with a precision which was comparable to the difference in IP measurements obtained from nearby sampling sites.

Arithmetic average IP concentrations at IP Network sites were predicted from TSP concentrations to within ±20% for all size-selective inlet IP maxima and for 89% of the dichotomous sampler IP maxima. This degree of uncertainty may be adequate for estimating IP averages for compliance purposes in certain situations.

Maximum IP concentrations at IP Network sites were predicted from TSP concentrations to within ±20% for 77% of the size-selective inlet IP maxima and for 60% of the dichotomous sampler IP maxima. The uncertainty associated with predicting maximum concentrations was comparable to that associated with predicting any concentration, irrespective of its magnitude.

IP and FP Composition and Sources

The chemical compositions of total, fine and coarse suspended particulate matter concentrations from sites in Buffalo, NY, Houston, TX, El Paso, TX, Philadelphia, PA and in the Bridesburg industrial area of Philadelphia were studied to identify and quantify likely source contributions to the fine and coarse particulate matter fractions. Microscopic analysis of the coarse fractions of several samples was performed-to identify source contributions.

The identification of likely contributors based on the geographical proximity of a major source to a receptor identified from emission inventories and site survey was often confirmed by chemical concentration measurements and receptor model source contribution calculations.

The chemical element balance and microscopic properties balance receptor models exhibited major limitations. Despite these limits it appears that major contributors to IP Network sites in the eastern United States for the periods under study were: unaccounted-for sulfate (possibly from the conversion of SO_2) and motor-vehicle exhaust in the average fine particle fraction and geological material and possibly biological material in the average coarse particle fraction. Industrial point sources showed small (less than 1 ug/m^3) contributions to both size fractions at urban-scale sites in most cases. Data were insufficient to apply these observations to western sites.

In an industrial neighborhood, where a number of sources were located in close proximity to each other and to the IP Network samplers, the average source contributions to the coarse fraction varied between sites even though the average inhalable particulate matter mass concentrations were roughly the same. A receptor model approach to quantifying source contributions in such a neighborhood may require more than one sampling site.

In general, the IP Network has accomplished its goals of providing a data base from which certain observations can be made and hypotheses can be formed. The data included in this report, however, are too limited to draw conclusions and many of the interpretation efforts made here should be applied again when the data base is more complete. If some of the recommendations of this report concerning IP Network sampling, analyses and reporting are put into effect, the value of the data base to researchers will be increased substantially.

CHAPTER 1

INTRODUCTION

The primary National Ambient Air Quality Standards for suspended particulate matter were established with the Clean Air Act of 1970. The sampling methods and values of these standards were based on the best technical information available at that time concerning the quantification of total suspended particulate matter (TSP, the mass per unit volume of particles with aerodynamic diameters less than approximately 30um) concentrations (Federal Register, 1971) and the effects of those concentrations on public health (U.S. HEW, 1969).

The state of knowledge concerning the ambient aerosol, its sampling and its adverse effects has advanced considerably in the past decade. The Clean Air Act Amendments of 1977 recognize the value of this increased knowledge in the modification of present standards:

> "Not later than December 31, 1980, and at five-year intervals thereafter, the Administrator shall complete a thorough review of the (air quality standard setting) criteria...and the (existing) national ambient air quality standards...and shall make such revisions in such criteria and standards and promulgate such new standards as may be appropriate..."(US House of Representatives, 1977, p. 7).

The National Ambient Air Quality Standards will be set based on a thorough review of the property damage and adverse health effects research. The first drafts of this review have been completed. The most important implication of the studies included in this review is that new standards for suspended particulate matter must be related to particle size as well as to mass concentration.

Miller et al (1979), after surveying experiments measuring the relative amounts of particulate matter deposited in different parts of the body as a function of particle aerodynamic diameter, concluded that:

> "...there is no standard conducting airway deposition curve, and hence, there appears to be no clear basis for establishing a particle size range which is exclusively restricted to the conducting airways."

They do note, however, that less than 10% of the particles with aerodynamic diameter greater than 15 um penetrate to trachea and state that:

> "...15 um would be a reasonable particle size cut-point to include in the design of a sampler which would differentiate particles deposited in the upper vs. lower respiratory tract."

Particles in the 2 to 15 um size range tend to deposit in the conducting airways of the respiratory system, while the majority of particles of aerodynamic diameter less than 2 um penetrate to the gas-exchange areas of the lungs. Though they recognize that this penetration is variable, Miller et al (1979) propose:

> "...a cut-point anywhere between 2 and 3 um would reflect particle deposition primarily associated with the gas-exchange areas of the lung..."

The exact size ranges to be monitored and the maximum concentrations to be allowed by a new set of standards have not yet been specified. The Clean Air Scientific Advisory Committee of the Science Advisory Board of U.S.EPA recommended in its meeting of July 29, 1981 that a 10 um upper size limit be used in establishing standards to protect public health. While this recommendation is not binding, it provides a reason to more thoroughly evaluate aerosol concentrations in the 0 to 10 um size range as well as those in the 0 to 15 um range.

Until the new standards are issued, the identifier applied to the mass concentration in the 0 to 10 or 15 um aerodynamic diameter size range is inhalable particulate matter (IP). The name given to mass concentrations in the 0 to 2.5 um aerodynamic size range is fine particulate matter (FP).

When a standard is promulgated, EPA's Office of Air Quality Planning and Standards (OAQPS) must direct the state and local agencies responsible for compliance monitoring to collect data appropriate for judging whether or not an area is in attainment of the standards. The states, in turn, must propose particulate matter emissions reductions which will bring the areas into attainment. When the standards are promulgated, sampling equipment specifications, sampler siting, and sampling frequencies must all be tailored to the acquisition of data compatible with those standards. Both areas in attainment and in violation of the present standard must gain an understanding of their status under the new standard. Areas with approved control strategy implementation plans must predict the efficacy of those plans for meeting the requirements of the new standards.

To understand these regulatory and monitoring aspects of a size-classified suspended particulate matter standard further, the Environmental Protection Agency's Environmental Monitoring and Support Laboratory has deployed an Inhalable Particulate Matter Sampling Network in key regions of the United States (Rodes, 1979). Ninety-six sampling stations came on line in 1979, with additional sites added in 1980 and 1981. This network was designed to sample IP in the 0 to 15 um size range. Since its deployment, size-selective sampling inlets have been developed and are being tested which will sample IP in the 0 to 10 um size range. When field tests are complete and commercial manufacturers provide a sufficient number of these inlets, IP data in the 0 to 10 um size range will be acquired at existing IP Network sites. In the interim, estimates of these concentrations will have to be made from the 0 to 15 um data.

This Inhalable Particulate Network measures particulate matter concentrations in three size ranges (0 to 30 um, 0 to 15 um and 0 to 2.5 um). Its coverage is meant to be representative of geographical, climatological, emissions and population areas in the United States, but it is not as extensive in space and time as the existing HIVOL compliance network. Sampling frequency is every 3 or 6 days.

The data from this network include mass concentrations of total, inhalable and fine suspended particulate matter (TSP, IP and FP, respectively). Selected samples are submitted to chemical analysis to determine elemental and ionic concentrations for TSP, IP, and FP fractions. Several special sampling studies have been undertaken.

The purpose of this study is to begin to answer a specific set of questions about fine and inhalable suspended particulate matter. These questions appear in Table 1.1; they are the questions most commonly asked by those who deal with air quality standards. They were posed by the network designers at EPA/OAQPS to guide the establishment and operation of the network.

A three-phase approach was used in this study:

The first phase resulted in a review of relevant literature related to the topic being addressed. This survey of past work was meant to suggest technical approaches to the interpretation of IP Network data, to evaluate the validity of those approaches, and to provide perspective to the conclusions drawn.

The second phase stated certain hypotheses related to the questions of Table 1.1 which could be confirmed or refuted using the IP Network data.

The third phase devised a model consistent with the IP Network data which supported or negated the hypotheses. If the data or the model were insufficient, then an assessment of the additional data or model development required was made.

It was not expected that all of these questions would be answered in their entirety in this report, or that the data collected in the IP Network would ultimately be sufficient to deal with them. Their statement here, however, sets several objectives to be accomplished. Where IP Network measurements were found insufficient to answer the questions, measurements from other studies were examined or new measurements were suggested which might reach those objectives in the future.

This report consists of ten chapters. The first, this introduction, explains the purposes and objectives of the study, the generalized technical approach, and previews what is to come in subsequent chapters. Chapters 2 through 4 are dedicated to the tenet that the interpretation of data should be done with an understanding of the process of acquiring those data. Environmental measurements

TABLE 1.1

QUESTIONS CONCERNING INHALABLE PARTICULATE MATTER

- SOURCES OF IP

  -What are the probable sources of inhaled particulate matter (IP) in urban areas; in rural areas?

  -What are the sources and the relative impact of particulate matter from: (a) exhaust from mobile sources (gasoline versus diesel), (b) stationary sources, (non-ducted versus ducted), (c) secondary particles (sulfates, nitrates, organics), and (d) fugitive dust sources such as re-entrained dust from paved versus unpaved roads on ambient inhaled particle levels?

  -What are regional differences in the sources of IP?

- MASS, CHEMICAL, ELEMENTAL AND SIZE CHARACTERIZATION

  -What are the differences and similarities in mass, size, elemental, and chemical composition concentrations from urban area to urban area, urban area to rural area, industrial city to non-industrial city, eastern versus western urban area, and heavily populated versus lightly populated areas?

  -What is the range and average of mass, size, elemental and chemical composition in these areas? How do mass concentrations of IP and FP relate to the TSP levels in these areas (ratio of FP and IP to TSP on both daily and annual basis)?

  -How do data from HIVOL, dichotomous sampler and size-selective HIVOL compare?

  -What are the causes of variations in the ratio of IP to TSP?

- SPATIAL PATTERNS

  -For an urban area, what is the spatial distribution of ambient IP concentrations? Are concentrations relatively uniform across an area (indicating uniform source contributions) or are there hot spots (indicating local source contributions)?

  -What are variations in IP concentrations among site types; by land use?

  -What is the vertical and horizontal distribution of IP near sources?

TABLE 1.1 (Continued)

-Are the gradients of IP significant with respect to instrument siting and control strategy development?

-What is the scale of representativeness of IP monitors and how many monitors would be needed for urban areas of various sizes?

- TEMPORAL PATTERNS

-What is the diurnal variation, weekday to weekend variation and seasonal variation of IP concentrations within an urban area?

-How does the chemical composition of IP change with each of these time periods?

- TRANSPORT/TRANSFORMATION/BACKGROUND

-Of the inhaled particulate matter measured in urban areas, how much is locally generated and how much is transported into urban areas from upwind sources?

-How much of this transported particulate matter is sulfate?

-What are the probable sources of sulfate particles in urban areas?

-How much sulfate is emitted directly as sulfate (primary sulfate) and what are the major sources of primary sulfate (e.g., oil fired power plants)?

-What is the origin of the sulfate being transported into the urban area?

-What is the scale of transport and where are the major concentrations (clusters) of the precursors located geographically?

-What is the impact of the Ohio River Valley on eastern U.S. IP levels?

-What are the particle removal processes and how do IP concentrations decrease as distance from the urban areas increases?

-What is the background level of IP on both a mass and chemical composition basis?

-What is the source of the material?

-How do background levels differ in various parts of the Nation?

tend to lose their identities once they enter a large computerized data bank. They seldom carry confidence intervals or information pertaining to their sampling and analysis.

Chapter 2 contains a detailed description of the aerosol sampler characteristics. Since any new particulate matter standard is likely to be size-specific, it is imperative that the particle size collection characteristics of aerosol samplers used to collect TSP, IP and FP are known. Wind tunnel tests have provided estimates of these characteristics and these tests show the variation of the particle size collection effectiveness of dichotomous samplers with wind speed. Integration of the product of collection effectiveness and typical concentrations in different size fractions of ambient aerosol allows the magnitude of this variation to be estimated. The comparability of 0 to 15 um and 0 to 10 um measurements is also evaluated by this method.

Chapter 3 presents the IP Network sampling process in detail, geographically locating the areas sampled and, to the extent which information is available, describing the sampling sites. Filter media, field sampling, filter handling and processing, chemical analysis, and data validation procedures are also summarized. Reproducibility of measurements via collocated sampling provides the best estimate of the precision to be attached to each value in the data base. An estimate of this precision is important to the comparison of one data value with another; if the confidence intervals around two measurements overlap, then there is no basis for finding any difference between them. This estimate is made in Chapter 3.

Most of the IP Network sampling sites are located in urban areas. To answer the questions in Table 1.1 about the sources of inhalable particulate matter and the effects of air movement, the types of sources in these urban areas and their locations with respect to the sampling sites should be specified. Eventually, all urban areas sampled by the IP Network need to identify the particulate matter sources and their locations if the sources of IP and FP concentrations are to be quantified. In Chapter 4 of this report, the character of the industrial sources and their relative location with respect to the IP sampling sites for some of those urban areas have been compiled. Average meteorological values related to air pollution have been tabulated. Previous studies of the source contributions to the different urban areas have been reviewed and summarized. This documentation will be referred to in later chapters to explain the results of ambient sampling.

Chapter 5 examines the spatial variability of size-classified aerosol concentrations with an eye toward relating those concentrations to sources and also to estimate the density of sampling sites required to represent a single land use area with one sampler.

The non-urban concentrations of size-classified suspended particulate matter is studied in Chapter 6. Data from the Sulfate Regional Experiment (SURE, Mueller and Hidy et al, 1981) and from non-urban sampling sites in the IP Network are compared to the concentrations in urban areas. The non-urban concentrations provide upper limits of aerosol mass transported into the urban areas.

The statistical distribution from which pollutant concentrations are drawn is an important consideration in estimating statistics from subsets of all possible data. Log-normal distributions have been used to describe air pollution data in the past. Several patterns of deviations from these distributions have been observed in the analysis of TSP concentrations from HIVOL samplers. In Chapter 7, these patterns are sought in the size-classified data from the IP Network and the validity of a log-normal distribution assumption to describe the data is evaluated. Geometric and arithmetic means are compared as reasonable statistics against which to evaluate a standard.

Until a more extensive network of size-classified monitoring sites is deployed, it will be necessary for many communities to estimate their IP concentrations from existing HIVOL TSP measurements. These estimates cannot be used to determine compliance with a standard -- only actual measurements can do that. These estimates would serve as guidance in network design and short-term planning. Chapter 8 derives a receptor-oriented model for relating IP to TSP concentrations and estimates the accuracy with which IP predictions can be made from HIVOL measurements. The usefulness of this model is evaluated against data from the Inhalable Particulate Network.

The major sources of IP and FP are not necessarily the same as the major sources of TSP. Yet the identification of IP and FP sources will become paramount as new control strategies are developed to meet new standards. In Chapter 9 the results of the previous chapters are combined with the results of chemical and microscopical analyses of special-study samples in a receptor-oriented model to quantify within specified confidence intervals the types of sources contributing to ambient size-classified aerosol concentrations.

Finally, Chapter 10 summarizes the work of all chapters. The limitations of the present data set with respect to answering the questions in Table 1.1 are pointed out. The requirements of future sampling and analyses necessary for obtaining more definitive answers are stated.

It is important to reiterate that while this report addresses the questions of Table 1.1 within the constraints of data from the Inhalable Particulate Network, it does not answer them all. The cost of designing experiments to address all of them was prohibitive. Difficulties in network start-up caused many size-classified samples to be missing or invalidated. Delays in data processing and analysis, and the time constraints imposed on the data interpretation phase of this project meant that much less than one year of data were reviewed from many sites. The majority of the interpretive efforts were dedicated to measurements acquired between May, 1979 and June, 1980. For some applications summary statistics from October, 1979 to September, 1980 were used. Size classifying inlets for 0 to 10 um monitoring were not available. The chosen sampler locations, sampling frequency and sample duration limited the information available for answering questions about spatial and temporal distributions. Many of the conclusions drawn from the technical approaches taken here are limited by this lack of completeness. As new and more complete data become available from the IP Network and other monitoring programs, they should be used to test the conclusions drawn in this report and to advance new ones. The hypotheses presented herein offer opportunities for some fascinating speculations about the distribution, transport and sources of suspended particulate matter in various size ranges in the United States. They remain to be tested, modified and retested to establish their veracity.

CHAPTER 2

AEROSOL SAMPLER
COLLECTION CHARACTERISTICS

The purpose of the IP Sampling Network is to create a data base of measurements as a function of particle size. The definition of the particle sizes collected depends on the instruments used for their collection. In this chapter the instruments used to obtain the samples from which the data in this study were derived are described. The particle size collection characteristics of different samplers which are intended to sample the same and different mass fractions of the total ambient aerosol are studied and compared. The results of the theoretical treatment are compared with a number of actual ambient measurements to evaluate their validity.

2.1 IP Network Sampler Configuration and Collection Effectiveness

Each sampling configuration was designed to include a standard 11 1/2" x 15" high volume (HIVOL) sampler, a HIVOL equipped with a 15 um size-selective inlet (SSI) and flow controller, and a Sierra 244, 244E or Beckman SAMPLAIR virtual impactor (also termed dichotomous sampler). Wedding (1980b) provides good illustrations of the SSI, Sierra and Beckman inlet constructions, while Dzubay and Stevens (1975) explain the operation of virtual impactors. All sites were equipped with HIVOL samplers. Due to technical and procurement difficulties, some sites possessed a HIVOL(SSI) without a dichotomous sampler, others had a dichotomous sampler without a HIVOL(SSI), while other sites had neither. The precise configuration at a given site is specified in Table A.1 of Appendix A as explained in Chapter 3. Where the lack of measurements from a missing sampler caused a significant effect on the interpretation process, that effect will be noted.

The sampling configuration was intended to measure Total, Inhalable, and Fine Suspended Particulate Matter concentrations. The definitions of Total, Inhalable and Fine Suspended Particulate Matter (Lioy et al, 1980) are:

- Total Suspended Particulate Matter (TSP): TSP is that portion of suspended material which is normally collected by a high-volume filter sampler for 24-hr and has 50% cut-size (the particle aerodynamic diameter at which one half of the particles penetrates the inlet and one half does not) ranging from 30 to 65 um for wind speeds between 2 to 24 km/hr. (McFarland et al, 1979)

- USEPA "Inhalable" Particulate Matter (IP): Miller et al (1979) proposed as "inhalable" dust that portion collected by a sampler with a 50% cut-size of 15 um. A similar definition would be the Thoracic Fraction (TF) since these are the particles that can enter the trachea and lungs and contribute toward the production of health effects generally associated with ambient particulate pollution, such as bronchial cancer, bronchitis and emphysema (Lippmann, 1980). More recent proposals impose a 50% cut-size of 10 um.

- Fine Particulate Matter (FP): FP is that portion of an aerosol which penetrates a particle collector with a 50% cut-size of 2.5 um. Depending on the penetration curve used for comparison (American Conference of Governmental Industrial Hygienists (ACGIH) or the British Medical Research Commission (BMRC)), FP could be nearly equal to, but generally smaller than the concentration known as the "respirable" fraction, which is defined by ACGIH and BMRC as the fraction which penetrates through the conductive airways of the lower respiratory tract (tracheobronchial tree) of healthy adults and is available for deposition in the nonciliated (alveolar) zone of the lung (Miller et al, 1979).

There is no sampling instrument which can collect all particles less than and no particles greater than a certain aerodynamic diameter. Only recently have standardized wind-tunnel methods been developed (Ortiz, 1978; McFarland et al, 1979b; Wedding et al, 1977) to measure the particle size collection characteristics of different aerosol sampling inlets under variable wind speed conditions. An understanding of these characteristics is central to the comparison and interpretation of inhalable particulate matter measurements.

The collection effectiveness curves of the sampling devices used in the IP Network are presented in Figures 2.1.1 and 2.1.2. Included in each diagram is the acceptable performance range suggested by EPA and reported by Ranade and Kashdan (1979) for sampling inhalable particulate matter.

Figure 2.1.1 also includes a collection effectiveness curve with a 50% cut-size of 10 um. This curve was obtained by shifting the

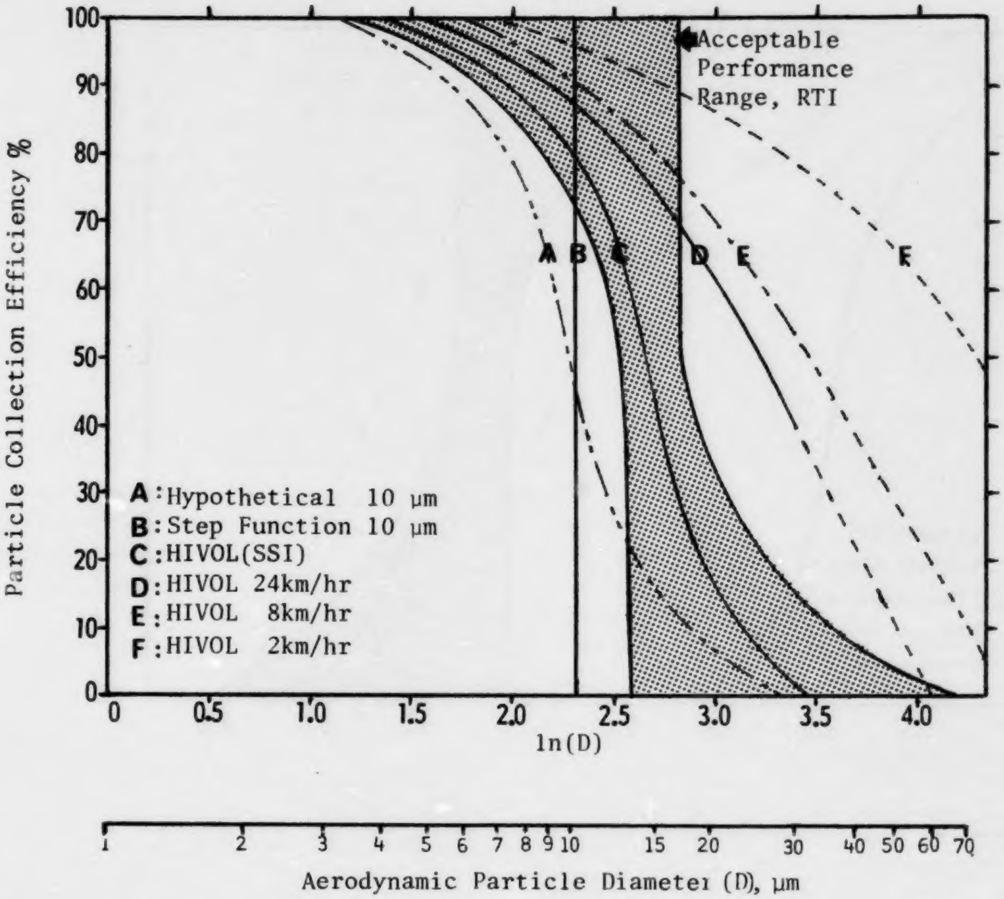

Figure 2.1.1 Collection Effectiveness of Standard HIVOL and HIVOL Size-Selective Inlets Under Various Wind Speeds (McFarland et al, 1979b). Logarithms of particle diameters are placed on the abscissa to facilitate reading of collection effectiveness as a function of ln D.

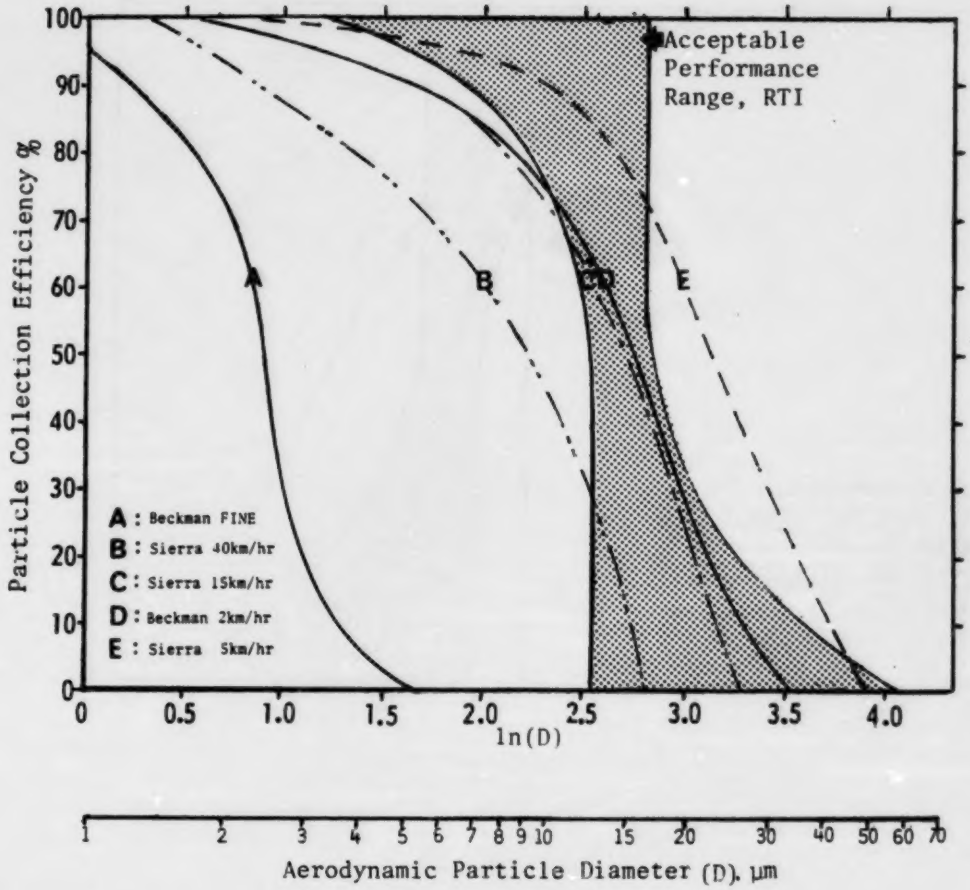

Figure 2.1.2 Collection Effectiveness of Beckman (MacFarland et al, 1979a) and Sierra 244 (Wedding et al, 1980a) Dichotomous Sampler Inlets. The Beckman SAMPLAIR collection effectiveness also varies with wind speed but only the 2km/hr curve was available.

15 um (HIVOL)SSI curve. The slope of the 10 um curve as defined by the parameter, s (McFarland et al, 1980b), is 1.35.

$$s = \frac{D_{.16}}{D_{.84}}$$

where

$D_{.16}$ = particle size for which collection effectiveness is 16%.
$D_{.84}$ = particle size for which collection effectiveness is 84%.

For comparison purposes, a perfect 10 um collection effectiveness curve with a slope equal to 1 is considered in Figure 2.1.1. The first item of note is that the collection effectiveness of the dichotomous sampler inlet and of the HIVOL sampler inlet are dependent on wind speed for aerodynamic particle diameters greater than 7 um. The tests done by Wedding et al (1980a) on the inlet to the Sierra 244 at 5 km/hr wind speeds and McFarland et al (1979a) on the Beckman SAMPLAIR inlet at 2 km/hr wind speeds are significantly different even though the designs of these inlets are similar. Simultaneous ambient sampling under the same wind speed conditions shows the measured mass concentrations collected through the two inlets to be different (Grantz, 1981). McFarland et al (1979a) measured 50% cut-sizes of 15.5, 13 and 10 um under wind speeds of 2, 8 and 24 km/hr, respectively, for the Beckman inlet while Wedding et al (1980a) measured 50% cut-sizes of 22, 15, and 9.5 um under wind speeds of 5 km/hr, 15 km/hr and 40 km/hr for the Sierra 244 inlet. These two tests show significant differences between collection effectiveness of dichotomous samplers under various wind speeds and between each other at similar wind speeds.

Though the methodologies of the Wedding and McFarland tests are essentially the same, they have not been demonstrated to be equivalent. A method of standardizing these tests needs to be developed. Wedding must test the Beckman inlet, McFarland must test the Sierra inlet and more simultaneous samples must be taken to resolve the discrepancy. This type of interlaboratory testing and simultaneous sampling should be carried out on all inlets which will be used in large scale sampling programs. The other possibility is that there are significant differences in the particle size collection characteristics of the Beckman and Sierra inlets.

McFarland et al (1979b) tests of the HIVOL collection characteristics show not only variability with wind speed; collection effectiveness also varies with wind direction because of the instrument's asymmetric design. At 20 km/hr wind speeds, the collection effectiveness of 23.5 um particles varies from 90% when the wind vector is perpendicular to one of the flat sides of the sampler, to 57% when the wind vector points to the corner of the HIVOL inlet.

The wind tunnel tests of the circular HIVOL size-selective inlet show its collection effectiveness to be virtually independent of wind speed. McFarland et al (1979b) measured a 15 um 50% cut-size under 2 km/hr, 8 km/hr and 24 km/hr wind speeds. Wedding (1980b) found 50% cut-sizes for the HIVOL(SSI) of 13.4, 14.4, and 12.5 um at the same respective wind speeds which differs from the McFarland tests to a lesser degree than that exhibited between the dichotomous sampler tests. This agreement for the HIVOL(SSI) inlet lends credence to the equivalency of the two wind tunnel tests and suggests that there may be significant differences between the Beckman and Sierra particle collection characteristics.

Because of the difference in collection effectiveness curves, IP data reporting should also include the sampler used to collect the measurements and typical wind speeds under sampling conditions. In this report, the operational definitions of aerosol samples will be:

- HIVOL: TSP collected by the HIVOL sampler irrespective of wind speed. Nominally 0 to 30 um size range.
- SSI: IP collected by the HIVOL equipped with a size-selective inlet. Nominally 0 to 15 um size range.
- TOTAL: IP expressed as the sum of FINE and COARSE concentrations collected with a Sierra 244 or Beckman SAMPLAIR dichotomous virtual impactor sampler, irrespective of wind speed. Nominally 0 to 15 um size range. The wind tunnel tests suggest that Beckman and Sierra samples should receive different designations. The EPA data base does not provide this information.

- FINE: FP collected by the fine stage of the dichotomous virtual impactor sampler and corrected for fine particulate matter which ends up on the COARSE filter. Nominally 0 to 2.5 um size range.
- COARSE: Coarse Particulate matter (CP) collected by the coarse stage of the dichotomous virtual impactor sampler and corrected for fine particulate matter, irrespective of wind speed. Nominally 2.5 to 15 um size range.

2.2 Collection Efficiencies of IP Network Samplers

Given the results of these wind tunnel tests, there is no doubt that different samplers under different ambient conditions measure different fractions of the total suspended particulate matter. The question of how much difference should be expected between simultaneous measurements with different instruments has been examined as follows.

The mass of particulate matter collected by a sampler in a particle size range is equal to the mass of the particulate matter in the air in that size range times the average collection effectiveness of the sampler over that range. If the ambient mass concentrations are distributed as a function F(D) of aerodynamic particle diameter, D, and the collection effectiveness of the sampler as a function of particle size is E(D) then the mass concentration, C, measured by the sampler is

$$C = \int_0^\infty F(D)\, E(D)\, dD \qquad 2\text{-}1$$

The particle size distribution, F, is also a function of space and time while E is also a function of wind speed. For the purposes of this discussion, these variables will be held constant for calculating values of C.

The effectiveness of the IP Monitoring Network inlets, E(D), are presented in Figures 2.1.1 and 2.1.2. It remains to choose an appropriate particle size distribution function, F(D).

Atmospheric aerosols have been observed to have a bimodal mass distribution (Junge, 1963; Whitby, 1978; Whitby and Sverdrup, 1980; Brock, 1973; Lundgren and Paulus, 1975) with a minimum in the neighborhood of 2 um. Those particles less than 2 um in aerodynamic diameter can be broadly classifed as fine and those with diameters greater than 2 um are termed coarse. There is further evidence of these modes being log-normal and additive. Fine aerosols are generated primarily by condensation while coarse aerosols are produced for the most part by mechanical processes.

Whitby and Sverdrup (1980) fitted three additive log-normal functions to atmospheric aerosol measurements made with optical particle counters. These fits of additive log-normal distributions to ambient measurement were found to be applicable under a variety of circumstances as evidenced by low reduced chi-squares statistics. Whitby and Sverdrup (1980) formulated seven different categories into which their hundreds of fitted distributions fell. In all of these categories, more than 90% of the aerosol volume was concentrated in the superposition of two log-normally shaped modes. Lundgren and Paulus (1975) also found atmospheric aerosols to have bimodal mass distributions which could be fitted by two additive log-normal distributions.

The fine and coarse modes have been observed to have geometric mean diameters in the range of .2 to .7 um and 3 to 30 um, respectively. The geometric mean diameter and geometric standard deviation for selected categories are listed in Table 2.2.1.

The atmospheric aerosol mass distribution, assuming it to be additive bimodal log-normal, may be represented by

$$F(D) = \frac{1}{\sqrt{2\pi}} \left\{ \frac{P}{\ln \sigma_f} e^{-\left(\frac{(\ln D - \ln D_f)^2}{2 \ln^2 \sigma_f}\right)} + \frac{(1-P)}{\ln \sigma_c} e^{-\left(\frac{(\ln D - \ln D_c)^2}{2 \ln^2 \sigma_c}\right)} \right\} \tag{2-2}$$

where

P = the fractional mass in the fine mode and $1-P$ is the fractional mass in the coarse mode

D = particle aerodynamic diameter

TABLE 2.2.1

GEOMETRIC MEAN AERODYNAMIC DIAMETERS AND GEOMETRIC STANDARD DEVIATIONS FOR SELECTED ATMOSPHERIC PARTICLE SIZE DISTRIBUTIONS

Aerosol Classification	Fine Mode: Geometric Mean Aerodynamic Diameter D_f (um)	Fine Mode: Geometric Standard Deviation σ_f	Coarse Mode: Geometric Mean Aerodynamic Diameter D_c (um)	Coarse Mode: Geometric Standard Deviation σ_c
Average[a]	.38	2.02	10.20	2.26
Urban Average[b]	.50	5.0	20.00	2.00
Background and Aged Urban Plume[a]	.47	1.84	7.27	2.12
Marine[a]	.39	2.0	19.30	2.70

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[a] Whitby and Sverdrup (1980). Optical diameters, D_o, reported in this reference have been converted to aerodynamic diameters, D_a, by $D_a = \sqrt{\rho} \times D_o$ where a density, ρ, of 1.7 gm/cm^3 has been used for the fine mode and 2.6 gm/cm^3 has been used for the coarse mode. While this approximation may not be true in all cases, it is legitimate for making comparisons between the collection efficiencies of different samplers under a variety of circumstances.

[b] Lundgren and Paulus (1975).

D_f & D_c = the geometric mean aerodynamic diameters for the fine and coarse modes, respectively

σ_f & σ_c = the geometric standard deviations for the fine and coarse modes, respectively.

The parameters P, D_f, D_c, σ_f and σ_c in Table 2.2.1 are fitted by minimizing the sums of the squares of the differences between F(D), integrated over the same size range as an ambient measurement, and the fraction of the total mass measured in that size range. Equation 2-2, with appropriate parameters is an appropriate F(D) to be used in Equation 2-1.

The integral of Equation 2-1 was calculated by dividing the interval from 0 to 100 um into regions over which the natural logarithm of the particle diameter was equal to .2 . For the ith interval

$$C_i = F(D_i)E(D_i)\Delta \ln D \qquad 2\text{-}3$$

$$= .2\ F(D_i)E(D_i)$$

The particle diameter at which F(D) was evaluated via Equation 2-2 was chosen as the center of the interval. E(D) was read from the curves of Figures 2.1.1 and 2.1.2 at the same value of ln D.

The summation of fractional mass concentrations, ΣC_i, over all intervals between 0 and 100 um gives the fraction of the total mass collected by the inlet under consideration. The maximum error introduced by numerical approximation over the intervals was estimated to be less than 3% by dividing a few intervals with the most rapid change of F(D)E(D) into smaller intervals and comparing the integrals with those obtained for the larger interval.

Other sources of errors in this treatment result from the simplification with respect to real aerosol size distributions inherent in equation 2-1, measurement uncertainties of the collection effectiveness curves, and the lack of consideration of mass measurement interferences (two such interferences, artifact formation and passive deposition, are identified in Chapter 3 as agents which could affect the mass measured by IP Network samplers). For the present analysis these errors are noted, but not quantified. Limitations imposed on the conclusions because of these shortcomings will be noted where appropriate.

The collection efficiency of the sampler (i.e. mass collected by inlet/total suspended mass) for the size distributions specified by the parameters in Table 2.2.1 and the collection effectiveness curves in Figures 2.1.1 and 2.1.2 were calculated and are presented in Table 2.2.2. The fine particle fraction, P, of the total mass was set equal to .33 and .5 for these calculations. This study and others show this to represent a reasonable ambient range.

A close examination of the results in Table 2.2.2 provides some important insights into the variability of the different IP Network sampler inlets, and two hypothetical 10 um inlets, with respect to particle size distributions, wind speeds, and the proposed acceptable performance range for 15 um inlets.

The collection efficiencies of all inlets under all wind speed conditions vary with particle size distribution. The efficiencies increase as the total aerosol mass is shifted toward the smaller particles because the collection effectiveness increases as particle size decreases. The lowest efficiencies are obtained for the urban average and marine distributions, which Table 2.2.1 shows to have the largest geometric mean aerodynamic particle diameters (approximately 20 um) in the coarse mode. At average wind speeds of 8 to 15 km/hr expected at IP Network sites, TOTAL collection efficiencies range from .52 to .87, SSI efficiencies range from .55 to .89, and HIVOL efficiencies range from .76 to .96 for the size distributions considered. The size distribution which is the most representative of the majority of IP Network sites is probably the urban average (Lundgren and Paulus, 1975) with P = .33. For this distribution, the TOTAL, SSI and HIVOL collection efficiencies at typical wind speeds are .52, .55 and .76, respectively.

The variation of sampler collection efficiency with wind speed is most pronounced for the TOTAL and HIVOL samplers. For the urban average size distribution (P = .33) the collection efficiency of the

TABLE 2.2.2

THEORETICAL COLLECTION EFFICIENCIES FOR DIFFERENT
AEROSOL SAMPLER INLETS AND DIFFERENT COLLECTION EFFECTIVENESS CURVES FOR TYPICAL SIZE DISTRIBUTIONS

Aerosol Classification[a]	% Fine	Sierra SAMPLERS			HIVOL SAMPLERS			Beckman	HIVOL[d] (SSI)	Hypothetical[d] 10um		Lower[e] Envelope	Upper[e] Envelope
		Wind speed 5 km/hr	15 km/hr	40 km/hr	Wind speed 2 km/hr	8 km/hr	24 km/hr	Wind speed 2 km/hr		(slope = 1.35)	(slope = 1.0)		
Average[b]	33	.85	.73	.63	.95	.89	.85	.74	.76	.66	.57	.69	.89
	50	.88	.80	.72	.96	.92	.89	.80	.82	.74	.67	.77	.91
Urban average[c]	33	.67	.52	.42	.89	.76	.70	.55	.55	.45	.37	.47	.71
	50	.75	.63	.56	.92	.82	.77	.65	.66	.58	.52	.59	.78
Background and Aged Urban Plume[b]	33	.92	.83	.73	.97	.94	.91	.82	.85	.76	.67	.79	.95
	50	.94	.87	.80	.98	.96	.93	.87	.89	.82	.75	.85	.96
Marine[b]	33	.70	.59	.51	.89	.77	.72	.60	.61	.53	.47	.55	.73
	50	.77	.69	.63	.92	.83	.79	.70	.71	.65	.60	.66	.80

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[a] See Table 2.2.1 for aerosol classification.

[b] Whitby and Sverdrup (1980).

[c] Lundgren and Paulus (1975).

[d] Collection efficiencies are independent of wind speed.

[e] Collection efficiencies which would be achieved by inlets with effectiveness curves corresponding to the lower and upper limits of Ranade and Kashdan (1979).

TOTAL sampler decreases from .67 to .42 as wind speeds rise from 5 km/hr to 40 km/hr. These extremes represent variations of +29% and -19% with respect to the collection efficiency under typical (~15 km/hr) wind speed conditions. For the HIVOL sampling the same size distributions, efficiencies decrease from .89 to .70 as wind speeds increase from 2 km/hr to 24 km/hr. These extremes constitute +17% and -8% deviations with respect to typical wind speed conditions.

The upper and lower collection efficiencies of the proposed acceptable performance range (Ranade and Kashdan, 1979) for 15 um inlets offer a considerable range for possible collection efficiencies. The acceptable performance range exhibits +29% and -15% deviations with respect to the SSI collection effectiveness curve, which falls in the center of the range (see Figure 2.1.1).

The dichotomous sampler (both Sierra and Beckman) and the SSI collection efficiencies fall within the efficiency limits of the acceptable performance range regardless of the size distribution sampled and the wind speed with the exception of the Sierra sampler under 40 km/hr wind speeds. This is in contrast to their collection effectiveness curves illustrated in Figures 2.1.1 and 2.1.2 for which only the SSI sampler meets the criteria.

HIVOL collection efficiencies are marginally within those corresponding to the upper limit of the acceptable performance range under 24 km/hr wind speed conditions, but they exceed this limit for all size distributions in 2 km/hr and 8 km/hr winds.

Both of the hypothetical 10 um inlets exhibit collection efficiencies less than that of the lower boundary of the acceptable performance range for 15 um inlets.

The predicted collection efficiencies for the HIVOL (ranging from 70 to 96%) are generally lower than the 97% ± 3% observed by Lundgren and Paulus (1975). The apparent reduction in overall collection efficiency could be due to:

- Mass measurement interferences (e.g. passive deposition and artifact formation) not included in the model
- The error introduced by the bimodal log-normality assumption

- Errors due to the extension of the HIVOL collection effectiveness curve beyond the experimental data points
- The HIVOL collection effectiveness curve generated with the use of uniform oil droplets (McFarland et al, 1980) not being quite the same as that of the airborne particles sampled by Lundgren and Paulus (1975)

No data on the absolute collection efficiencies of the dichotomous samplers and the HIVOL size selective inlets under ambient conditions have yet been acquired.

2.3 Relative Collection Efficiencies of Different Sampler Inlets

Each of the IP sampler collection effectiveness curves is distinct from every other, but the collection efficiencies listed in Table 2.2.2 are much more similar than would be initially suspected by comparing the effectiveness curves. This is so because typically a third to half of the mass in the aerosol size distributions examined is in the size region where the collection effectiveness of the samplers is close to 100%.

Three inter-sampler collection efficiency comparisons are relevant to the interpretation of IP Network data:

1. IP inlets (both dichotomous sampler and HIVOL size-selective inlets) to the standard HIVOL inlet
2. Dichotomous sampler inlets to the HIVOL size-selective inlet
3. The hypothetical 10 um inlets to dichotomous sampler and HIVOL size-selective inlets

The first comparison is important because of the plethora of HIVOL measurements available and the desire to develop a predictive model allowing IP concentrations to be predicted from TSP data. Such a model is formulated in Chapter 8 of this report. The fraction of measured TSP which would be measured as IP by the network samplers under various wind speeds and particle size distributions can be estimated by this comparison and is given in Table 2.3.1.

For the SSI measurements, which show no wind speed dependence, this ratio increases with increasing wind speeds. In contrast, for the TOTAL measurements with the Sierra dichotomous sampler, the ratios

TABLE 2.3.1

RATIOS OF IP SAMPLER COLLECTION EFFICIENCIES TO HIVOL COLLECTION EFFICIENCIES AS A FUNCTION OF WIND SPEED AND PARTICLE SIZE DISTRIBUTION

Relative[a] IP Collection Efficiencies With Respect to HIVOL

		SSI/HIVOL			TOTAL/HIVOL (Beckman)	TOTAL/HIVOL (Sierra)			
Aerosol Classification[b]	% Fine	2 km/hr	Wind speed 8 km/hr	24 km/hr	Wind speed 2 km/hr	5 km/hr[c]	Wind speed 15 km/hr[c]	40 km/hr[d]	Ranges of Ratios
Average (Whitby)	33	.80	.85	.89	.78	.96	.82	.74	.74 to .96
	50	.89	.91	.92	.83	.96	.87	.81	.81 to .96
Urban Average (Lundgren)	33	.62	.72	.79	.62	.88	.68	.60	.60 to .88
	50	.72	.80	.86	.71	.91	.77	.73	.71 to .91
Background (Whitby)	33	.88	.90	.93	.85	.98	.88	.80	.80 to .98
	50	.91	.93	.96	.89	.98	.91	.86	.86 to .98
Marine (Whitby)	33	.69	.79	.85	.67	.91	.77	.71	.67 to .91
	50	.77	.86	.90	.76	.93	.83	.80	.77 to .93

---

[a] Sampler efficiencies at the same or similar wind speeds are compared.

[b] See Table 2.2.1 for aerosol classification.

[c] Compared to 8 km/hr HIVOL efficiency.

[d] Compared to 24 km/hr HIVOL efficiency.

decrease with increasing wind speeds. These ratios also depend on the particle size distribution being sampled; at typical wind speeds of 8 km/hr and 15 km/hr, the SSI/HIVOL ratios range from .72 to .93 while corresponding TOTAL/HIVOL ratios extend from .68 to .91. For the urban average (P = .33) distribution at typical wind speeds, the SSI/HIVOL ratio is .72 and the TOTAL/HIVOL ratio is .68.

The second comparison demonstrates the extent to which inlets on samplers which are intended to measure the same fraction of the aerosol mass, the IP fraction, can be expected to do so. The ratios of collection efficiencies of these samplers tabulated in Table 2.3.2 show the degree of equivalency which can be expected under ambient measurement conditions. As seen in the Table 2.3.2, the ratio of collection efficiency of dichotomous samplers to HIVOL(SSI) is close to, but generally less than 1.0. For the typical 15 km/hr wind speed and urban average size distribution, the samplers measure the same mass concentrations within 5% of each other. There is a discrepancy, as noted earlier, between the Beckman and Sierra inlets at low wind speeds; the Sierra inlet samples up to 22% more aerosol mass than the Beckman or SSI according to these tests. At high wind speeds, a substantial difference, approaching 25% between TOTAL and SSI samples, is apparent. To reiterate, this treatment involves only the penetration properties of the inlet and does not consider the adsorption or loss of gases by the filter media or passive deposition on filters during sampler standby periods prior to and after sampling.

The final comparison is important to relate conclusions drawn from a measurement system with a 15 um cut-size to a standard which would possibly address the mass fraction in the 0 to 10 um size range. The ratios of the hypothetical 10 um inlet (s = 1.35) collection efficiencies to the TOTAL and SSI efficiencies appear in Table 2.3.3. For the urban average aerosol (P = .33) and 15 km/hr wind speeds the 10 um inlet would collect 87% of the mass collected by a Sierra dichotomous sampler and 82% of the mass collected by a HIVOL with a size-selective inlet. These factors, rounded to reflect their uncertainties, .9 for TOTAL measurements and .8 for SSI measurements, can be used to estimate mass concentrations in the 0 to 10 um size range from existing IP measurements. These factors must be used with

TABLE 2.3.2

RATIOS OF DICHOTOMOUS SAMPLER COLLECTION EFFICIENCIES TO HIVOL SIZE-SELECTIVE INLET COLLECTION EFFICIENCIES AS A FUNCTION OF WIND SPEED AND PARTICLE SIZE DISTRIBUTION

TOTAL/SSI

		(Sierra)			(Beckman)	
		Wind speed				
Aerosol Classification	% Fine	5 km/hr	15 km/hr	40 km/hr	2 km/hr	Ranges of Ratio
Average (Whitby)	33	1.12	.96	.83	.97	.83 to 1.12
	50	1.07	.98	.88	.98	.88 to 1.07
Urban Average (Lundgren)	33	1.22	.95	.76	1.00	.76 to 1.22
	50	1.14	.95	.85	.98	.85 to 1.14
Background (Whitby)	33	1.08	.98	.86	.96	.86 to 1.08
	50	1.06	.98	.90	.98	.90 to 1.06
Marine (Whitby)	33	1.14	.97	.84	.98	.84 to 1.14
	50	1.08	.97	.89	.99	.89 to 1.08

TABLE 2.3.3

RATIOS OF HYPOTHETICAL TEN MICRON INLET COLLECTION EFFICIENCIES TO IP SAMPLER COLLECTION EFFICIENCIES AS A FUNCTION OF WIND SPEED AND PARTICLE SIZE DISTRIBUTION

(Slope of 10 um collection effectiveness curve is 1.35)

		10 um/TOTAL (Sierra)			10 um/Total (Beckman)	10 um/SSI	
		Wind Speed					
Aerosol Classification	% Fine	5 km/hr	15 km/hr	40 km/hr	2 km/hr		Range of Ratios
Average (Whitby)	33	.78	.90	1.05	.89	.87	.78 to 1.05
	50	.84	.93	1.03	.93	.90	.84 to 1.03
Urban average (Lundgren)	33	.67	.87	1.07	.82	.82	.67 to 1.07
	50	.77	.92	1.04	.88	.88	.77 to 1.04
Background and Urban Plume (Whitby)	33	.83	.92	1.04	.93	.89	.83 to 1.04
	50	.87	.94	1.03	.94	.92	.87 to 1.03
Marine (Whitby)	33	.76	.90	1.04	.88	.87	.76 to 1.04
	50	.84	.94	1.03	.93	.92	.84 to 1.03

great care, however, with full recognition of the range of values they can take under different wind speed conditions and aerosol size distributions. It appears that the present IP Network sampling configuration overestimates 0 to 10 um mass concentrations by 10% to 20%.

2.4 The SURE Sampling Inlet Characteristics

Several other samplers can be said to measure FP and IP. Not all have undergone wind tunnel characterization and it is inappropriate to examine them here. Lioy et al (1980) and Camp et al (1978) mention several of them. The sequential filter sampler designed especially for the Sulfate Regional Experiment (SURE, Mueller and Hidy et al, 1981) is important because it acquired time-resolved (3-hr samples, 8 samples/day) of IP and FP at nine sites in non-urban areas of the eastern United States during 1977 and 1978. Some of these data will be summarized in Chapter 6 to assess non-urban concentrations of IP and FP, so it is important to relate the collection characteristics of these samplers to those in the IP Network.

The collection effectiveness curves at different wind speeds for the SURE IP and FP samplers are given in Figure 2.4.1. The IP 50% cut-size is 9 ± 3 um, depending on wind speeds. Table 2.4.1 compares the SURE IP collection efficiencies with those of the HIVOL, SSI and hypothetical 10 um inlets.

Most of the SURE sampler collection efficiencies at 2 km/hr and 8 km/hr wind speeds are at or slightly below the lower limit of the acceptable performance range for 15 um inlets; the collection efficiencies at 24 km/hr are significantly less than this lower limit. The variability of collection efficiency with respect to particle size distributions and wind speeds is similar to that exhibited by the Sierra dichotomous samplers in Table 2.2.2. For the size distributions studied, the SURE IP sampler should yield mass concentrations equal to 80% to 90% of those which would be measured by a Sierra sampler. Since all SURE sites were non-urban, with average wind speeds of 10 to 15 km/hr, the efficiencies calculated for the background and urban plume ($P' = .50$) size distribution at 8 km/hr for the SURE sampler and 15 km/hr for the Sierra sampler provide the most

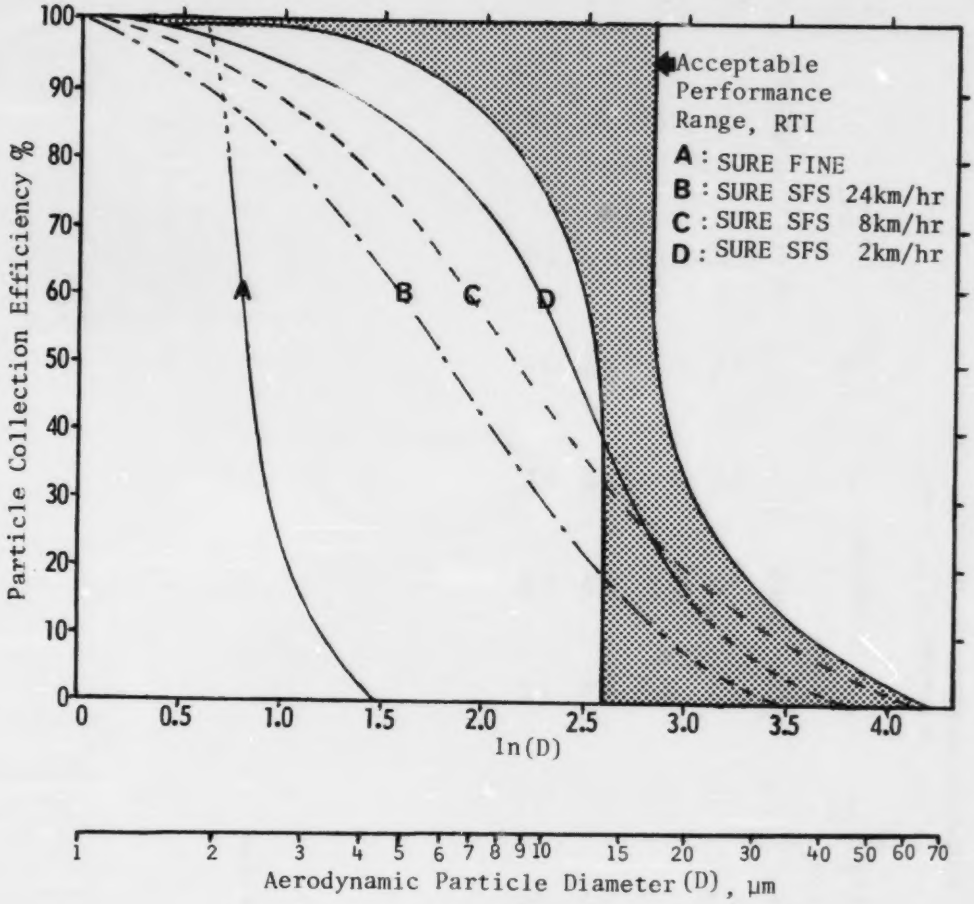

Figure 2.4.1 Collection Effectiveness of the SURE Sampler, Flow Rate 130 l/m^3 (McFarland et al, 1980)

TABLE 2.4.1

THEORETICAL COLLECTION EFFICIENCIES FOR SURE SFS, SSI, AND HYPOTHETICAL 10 um INLETS

Aerosol Classification[a]	% Fine	SURE SFS SAMPLERS Wind speed 2 km/hr	 8 km/hr	 24 km/hr	HIVOL SAMPLERS Wind speed 2 km/hr	 8 km/hr	 24 km/hr	HIVOL[d] (SSI)	Hypothetical[d] 10um (slope=1.35)	 (slope=1.10)	Lower Envelope[e]	Upper Envelope[e]
Average[b]	33	.68	.63	.55	.95	.89	.85	.76	.66	.57	.69	.89
	50	.76	.72	.66	.96	.92	.89	.82	.74	.67	.77	.91
Urban average[c]	33	.50	.48	.40	.89	.76	.70	.55	.45	.37	.47	.71
	50	.61	.59	.53	.92	.82	.77	.66	.58	.52	.59	.78
Background and Urban Plume[b]	33	.76	.70	.62	.97	.94	.91	.85	.76	.67	.79	.95
	50	.82	.78	.72	.98	.96	.93	.89	.82	.75	.85	.96
Marine[b]	33	.56	.54	.48	.89	.77	.72	.61	.53	.47	.55	.73
	50	.67	.66	.61	.92	.83	.79	.71	.65	.60	.66	.80

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[a] See Table 2.2.1 for aerosol classification.

[b] Whitby and Sverdrup (1980).

[c] Lundgren and Paulus (1975).

[d] Collection efficiencies are independent of wind speed.

appropriate comparison; in these cases the SURE samples would measure aerosol mass concentrations equal to 90% of simultaneous Sierra sampler measurements and 88% of simultaneous SSI measurements.

The SURE collection efficiencies at 8 km/hr most closely approximate the hypothetical 10 um inlet (s = 1.35) of all inlets evaluated here. For the urban average size distribution (P = .33), the SURE measurement would exceed the 10 um measurement by 7% whereas for the background and aged urban plume distribution (P = .50), it would be 5% less than the 10 um measurement.

Because the uncertainties resulting from the different sampling locations and sampling periods of SURE and IP Network measurements are expected to be greater than the 10% difference in mass collection efficiencies of SURE and dichotomous samplers, the two measures will be treated equivalently in this report.

The SURE and dichotomous FP collection effectiveness curves are nearly identical and intercomparison studies (Camp et al, 1978) between the SURE FP and earlier models of the dichotomous sampler show the mass concentrations measured to be equivalent.

The SURE data base presents a large quantity of size-classified concentration measurements with established accuracy and precision which can be used to characterize non-urban IP and FP concentrations in the eastern United States. The SURE IP measurements may more closely approximate those which would be made with a 10 um cut-size inlet than the IP Network measurements.

2.5 Comparison of Calculated and Measured Relative Collection Efficiencies

The collection effectiveness curves and the collection efficiencies derived from them in the previous sections are based on laboratory measurements and certain assumptions about size distributions which may not be valid under ambient sampling conditions. Since many IP Network sites ran HIVOL, SSI and TOTAL samples simultaneously, it is possible to compare the ratios of mass concentrations collected with these samplers to those presented in Tables 2.3.1 and 2.3.2.

These average ratios for TOTAL/HIVOL, SSI/HIVOL, and TOTAL/SSI for various site type classifications are tabulated in Tables 2.5.1, 2.5.2 and 2.5.3, respectively. Other researchers' measurements with the same types of samplers have also been tabulated (several other references with sampler comparison results were reviewed, e.g. Kolak and Visalli (1981), Camp et al (1978), Dzubay and Stevens (1975), Trijonis et al (1980), but results were not included because the sampling inlets differed from those used in the IP Network).

Three methods have been used to establish the relationships between simultaneous measurements of two samplers, the average ratio, the ratio of averages, and the slope of a linear regression between one measurement and the other. Results of each of these methods have been placed in Tables 2.5.1, 2.5.2, and 2.5.3 because, as can be seen for IP Network data used in this study, they are not the same. By listing all three relationships it is possible to compare the inter-sampler relationships of the IP Network with those of other networks. The average ratio should be compared with the calculated values in Tables 2.3.1 and 2.3.2. The final column in each one of Tables 2.5.1, 2.5.2, and 2.5.3 contains the calculated ratios which are closest to the measured ratios. The samplers, size distributions and wind speeds corresponding to these ratios are listed in the notes for each table.

The three TOTAL/HIVOL relationships in Table 2.5.1 show a substantial variability for the same data. For all site types combined, the linear regression slope is the lowest at .60 while the average ratio is the highest at .73. This trend persists for all site types. The linear regression slopes found in this analysis of IP Network data are consistent with those found by Suggs et al (1981b) (using measurements from the same network), Miller (1980), Wendt and Torre (1981), Pashel et al (1980) and Grantz (1981). The ratios of averages found by this study, Suggs, and Grantz are in reasonable agreement while those reported by Miller are approximately 25% lower than the others. The average ratios reported by Suggs are lower than those found in this study even though the basic data set is the same. This is due to the different methods of calculation and the different data validation procedures used (Section 3.4 of this report describes

TABLE 2.5.1

RELATIONSHIPS BETWEEN TOTAL AND HIVOL MASS CONCENTRATION MEASUREMENTS

Study and Samplers	Site Type	Average Avg.	Ratio Std.[a]	Ratio of Averages[b]	TOTAL/HIVOL[f] Linear Regression Slope	Inter-cept	Correlation	No. of Samples[c]	Most Similar Theoretical Ratios[d]
This Study (see	All site types	.73	.18	.64	.60	5.3	.90	1135	.71[h], .73[i],
Chapter 8)	Urban Industrial	.74	.14	.66	.63	6.8	.91	259	.72[h], .74[g],
Sierra 244,	Urban Commercial	.70	.18	.70	.54	8.4	.87	249	.71[h]
Beckman SAMPLAIR	Urban Residential	.77	.18	.62	.64	6.2	.88	87	.77[k]
and HIVOL	Suburban Commercial	.64	.18	.62	.55	5.0	.78	71	.62[l]
	Suburban Residential	.73	.16	.62	.63	4.5	.91	325	.71[l]
	Rural Agricultural	.81	.28	.69	.55	9.5	.92	88	.82[m]
Suggs et al (1981b)[e]	All site types	.66	.20	.63	[g]			62,64,72	.68[h]
Sierra 244,	Industrial	.66	.13	.60	[g]			18,16,15	.68[h]
Beckman SAMPLAIR	Commercial	.60	.13	.60	[g]			22,23,26	.60[o]
and HIVOL	Residential	.69	.28	.64	[g]			13,15,19	.68[n]
	Rural	.72	.27	.70	[g]			9,10,12	.71[h]
	Birmingham,Commercial	[g]		[g]	.62	3.6	.94	34	
Miller (1980)	Urban Commercial	[g]		.46	[g]			0,31,15	
Sierra 244	Urban Commercial	[g]		.56	[g]			0,35,20	
and HIVOL	Urban Commercial	[g]		.43	[g]			0,35,19	
Wendt and Torre (1981)	All site types	[g]		[g]	.59	0	.72	[g]	
Sierra 244,									
Beckman SAMPLAIR									
and HIVOL									
Pashel et al (1980)	Industrial	[g]		[g]	.64	.55	.87	10	
Sierra 244 and HIVOL	Industrial	[g]		[g]	.63	10.6	.75	52	
Grantz (1981)	Industrial, Sierra	[g]		.64	.52	6.8	.80	66,67,97	
Beckman SAMPLAIR,	Insudtrial, Beckman	[g]		.56	.59	.46	.92	45,47,97	
Sierra 244	Industrial, Sierra	[g]		.62	.52	5.1	.77	75,80,89	

[a] Arithmetic average and standard deviation of individual TOTAL/HIVOL ratios.

[b] Ratio of arithmetic average TOTAL and arithmetic average HIVOL concentrations.

[c] Number of data pairs for average ratio, ratio of averages, and linear regression. When three numbers appear, the final two refer to the ratio of averages. The second is the number of samples used to calculate the average TOTAL, the third is the number of samples used to calculate the average HIVOL.

[d] Taken from Table 2.3.1.

[e] These ratios were calculated using some of the same data used in this report without the data elimination process described in Section 3.4. Averages within each site grouping are arithmetic averages of average concentrations and ratios at the individual sites within the group.

[f] Depending on the filter media used for TOTAL or HIVOL sampling, adsorption or loss of nitrogen or sulfur containing gases may positively or negatively interfere with mass concentration measurements from these samplers.

[g] Not specified in reference. [h] Urban Average, P=.33, Beckman 2 km/hr. [i] Urban Average, P=.50, Sierra 40 km/hr. [j] Average, P=.33, Sierra 40 km/hr.

[k] Urban Average, P=.50, Sierra 15 km/hr. [l] Urban Average, P=.33, Beckman 2 km/hr. [m] Average, P=.33, Sierra 15 km/hr.
[n] Urban Average, P=.33, Sierra 15 km/hr. [o] Urban Average, P=.33, Sierra 40 km/hr.

TABLE 2.5.2

RELATIONSHIPS BETWEEN SSI AND HIVOL MASS CONCENTRATION MEASUREMENTS

Study	Site Type	Average Avg.	Ratio[a] Std.	Ratio[b] of Averages	SSI/HIVOL[f] Linear Regression Slope	SSI/HIVOL[f] Linear Regression Intercept	SSI/HIVOL[f] Linear Regression Correlation	No of[c] Samples	Most Similar[d] Theoretical Ratios
This Study	All Sites	.74	.13	.80	.64	5.2	.93	683	.72[h]
	Urban Industrial	.72	.13	.72	.58	9.9	.91	291	.72[h]
	Urban Commercial	.73	.12	.78	.72	0.9	.94	194	.72[h]
	Urban Residential	.69	.13	.99	.69	0.4	.95	33	.72,[h] .69[i]
	Suburban Industrial	.66	.09	.72	.62	4.6	.92	27	.62,[g] .69[i]
	Suburban Commercial	.68	.12	.68	.80	-7.0	.90	23	.69,[i] .72[h]
	Suburban Residential	.77	.20	.78	.84	-4.2	.96	96	.77,[k] .79[l]
Suggs et al (1981b)[e]	All Sites	.70	.10	.84	g			35,36,72	.72[h]
	Industrial	.69	.08	.69	g			12,12,15	.72[h]
	Commercial	.69	.07	.73	g			15,14,26	.72[h]
	Residential	.72	.09	.90	g			5,7,19	.72[h]
	Rural	.70	.12	.77	g			3,3,12	.72[h]
Wendt and Torre (1981)	All site types				.82	-11.1	.98	g	
Grantz (1981)	Industrial	g		.81	.76	2.4	.85	49,55,89	
	Industrial	g		.75	.78	-.89	.96	64,64,97	

[a] Arithmetic average and standard deviation of individual SSI/HIVOL ratios.

[b] Ratio of arithmetic average SSI and arithmetic average HIVOL concentrations.

[c] Number of data pairs for average ratio, ratio of averages, and linear regression. When three numbers appear, the final two refer to the ratio of averages. The second is the number of samples used to calculate the average SSI, the third is the number of samples used to calculate the average HIVOL.

[d] Taken from Table 2.3.1.

[e] These ratios were calculated using some of the same data used in this report without the data elimination process described in Section 3.4. Averages within each site grouping are arithmetic averages of average concentrations and ratios at the individual sites within the group.

[f] Depending on the filter media used for HIVOL or SSI sampling, adsorption of nitrogen or sulfur containing gases may positively or negatively interfere with mass concentration measurements from these samplers.

[g] Not specified.

[h] Urban Average, P=.33, 8 km/hr or P=.50, 2 km/hr.

[i] Marine, P=.33, 2 km/hr.

[j] Urban Average, P=.33, 2 km/hr.

[k] Marine, P=.50, 2 km/hr.

[l] Marine, P=.33, 8 km/hr or Urban Average P=.33, 24 km/hr.

TABLE 2.5.3

RELATIONSHIPS BETWEEN TOTAL AND SSI MASS CONCENTRATION MEASUREMENTS

Study	Site Type	Average Avg.[a]	Ratio[a] Std.	Ratio[b] of Averages	TOTAL/SSI[f] Linear Regression Slope	Intercept	Correlation	No. of[c] Samples	Most Similar[d] Theoretical Ratios
This Study	All Sites	.97	.24	.80	.82	5.5	.92	285,1509,771	.97[h]
	Urban Industrial	1.05	.18	.91	[g]			80,365,314	1.06[i]
	Urban Commercial	.97	.27	.89	[g]			73,306,205	.97[h]
	Urban Residential	1.02	.13	.63	[g]			8,97,37	1.0[j]
	Suburban Industrial	.84	.10	.78	[g]			22,90,27	.85[k]
	Suburban Commercial	.81	.27	.91	[g]			26,90,27	.83[m]
	Suburban Residential	.92	.20	.80	[g]			56,456,118	.95[l]
Suggs et al (1981b)[e]	All Sites	.81	.10	.75				27,64,36	.83[m]
7All Sites				.81	3.3	.88	388		
	Industrial	.91	.17	.87	[g]			8,16,12	.90[h]
	Commercial	.76	.25	.81	[g]			13,23,14	.76[o]
	Residential	.83	.39	.72	[g]			4,15,7	.83[m]
	Rural	.72	.07	.91	[g]			2,10,7	.76[o]
Shaw et al (1981)	Rural			.71	[g]			[g]	
Grantz (1981)	Industrial, Sierra			.85	[g]			0,67,64	
	Industrial, Beckman			.74	[g]			0,47,64	
	Industrial, Sierra			.76	[g]			0,80,55	

[a] Arithmetic average and standard deviation of individual TOTAL/SSI ratios.

[b] Ratio of arithmetic average TOTAL and arithmetic average HIVOL concentrations.

[c] Number of data pairs for average ratio, ratio of averages, and linear regression. When three numbers appear, the final two refer to the ratio of averages. The second is the number of samples used to calculate the TOTAL average, the third is the number of samples in the SSI average.

[d] Taken from Table 2.3.2.

[e] These ratios were calculated using some of the same data used in this report without the data elimination process described in Section 3.4. Averages within each site grouping are arithmetic averages of average concentrations and ratios at the individual sites within the group. Average ratios are the inverse of the SSI/TOTAL ratio reported in Suggs (1981b).

[f] Depending on the filter media used for TOTAL or SSI sampling, adsorption or loss of nitrogen or sulfur containing gases may positively or negatively interfere with mass concentration measurements from these samplers.

[g] Not specified in reference. [h] Average, P=.33, Beckman and Marine, 15 km/hr. Sierra [i] Background, P=.50, Sierra 5 km/hr.

[j] Urban Average, P=.33, Beckman 2 km/hr. [k] Urban Average, P=.50, Sierra 40 km/hr. [l] Urban Average, Sierra 15 km/hr. [m] Average, P=.33, Sierra 40 km/hr.

[n] Background, P=.50, Sierra 40 km/hr. [o] Urban Average, P=.33, Sierra 40 km/hr.

those procedures). This comparison of measurements from different researchers using the same samplers highlights the difficulty of determining an experimental relationship between the collection efficiencies of different samplers. The data chosen and the methods of summarizing those data must be carefully considered.

The calculated ratios summarized in the final column of Table 2.5.1 come from size distributions and wind speed conditions which are plausible for the site types. For example, urban average distributions with wind speeds from 2 to 15 km/hr exhibit calculated ratios very similar to those measured at urban industrial, commercial and residential sites. Similarly, for rural agricultural sites the ratio for the average size distribution at 15 km/hr is the most similar.

Substantial variability in the individual ratios exists, as evidenced by the large standard deviations (which range from .14 to .28 for different site types). This is reasonable since the size distributions and the wind speeds vary significantly for the periods of time and geographical distances over which the samples were taken. The close agreement between the calculated and measured ratios lends credence to the model of Section 2.2 and to the results of Section 2.3.

The three SSI/HIVOL relationships of Table 2.5.2 do not show the same trend as the TOTAL/HIVOL relationships. In this case, though the linear regression slopes are usually the lowest (except in the case of negative intercepts), the ratio of averages is greater than or equal to the average ratio. The calculated SSI/HIVOL ratios for the urban average size distribution with 2 to 8 km/hr wind speeds are in fair agreement with the average ratios measured at each site type.

The TOTAL/SSI relationship is an important one, since both of these samplers are being used to estimate inhalable particulate matter concentrations. The calculated ratios in Table 2.3.2 show that the calculated equivalency of the two samplers varies up to 24% with size distribution and wind speed, though TOTAL/SSI ratios under typical wind speed and particle size conditions are approximately .95.

Table 2.5.3 compares the IP Network measured average TOTAL/SSI ratios with the calculated ratios. Most average ratios are fairly close to unity, though the size of the standard deviations indicates a large amount of variability. This variability is evident from the scatterplot of simultaneous TOTAL and SSI measurements in Figure 2.5.1.

The measured ratios at suburban sites are significantly less than those at the urban sites and are similar to those calculated for unlikely size distributions and wind speed conditions for these sites. Most of the suburban measurements were made during 1980 whereas greater than half of the urban measurements were taken in 1979. Different SSI and HIVOL filter media were used during each year, and it appears that the adsorption of sulfur and nitrogen containing gases on the 1980 filter medium is significantly higher than that on the 1979 filter medium. Since the TOTAL filter medium remained the same, the TOTAL/SSI ratio would decrease in 1980 if this adsorption contributed to SSI mass measurements. It is impossible to quantify this effect since the filter medium used for individual samples is not reported with the measurements. The magnitude of this artifact is discussed in Chapter 3.

This lengthy treatment of the particle size collection characteristics is of great importance to the formulation of monitoring requirements for estimating compliance with a size-classified standard as well as interpreting IP Network measurements. The following observations are applicable to these subjects:

- Though dichotomous sampler inlets do not meet the stated collection effectiveness requirements of Ranade and Kashdan (1979), they do meet the collection efficiency requirements under typical wind speeds and particle size distributions. HIVOL(SSI) samplers attain both collection effectiveness and collection efficiency requirements. Criteria for particle size collection efficiency for acceptable sampling devices should be specified in addition to or in place of criteria for collection effectiveness. The efficiencies of samplers which would fall within the window of Ranade and Kashdan (1979) range from 47 to 71% for a typical urban size distribution. A sampler with an effectiveness curve designed to meet the lower limit would sample 66% of the mass of a sampler designed to correspond to the upper limit.

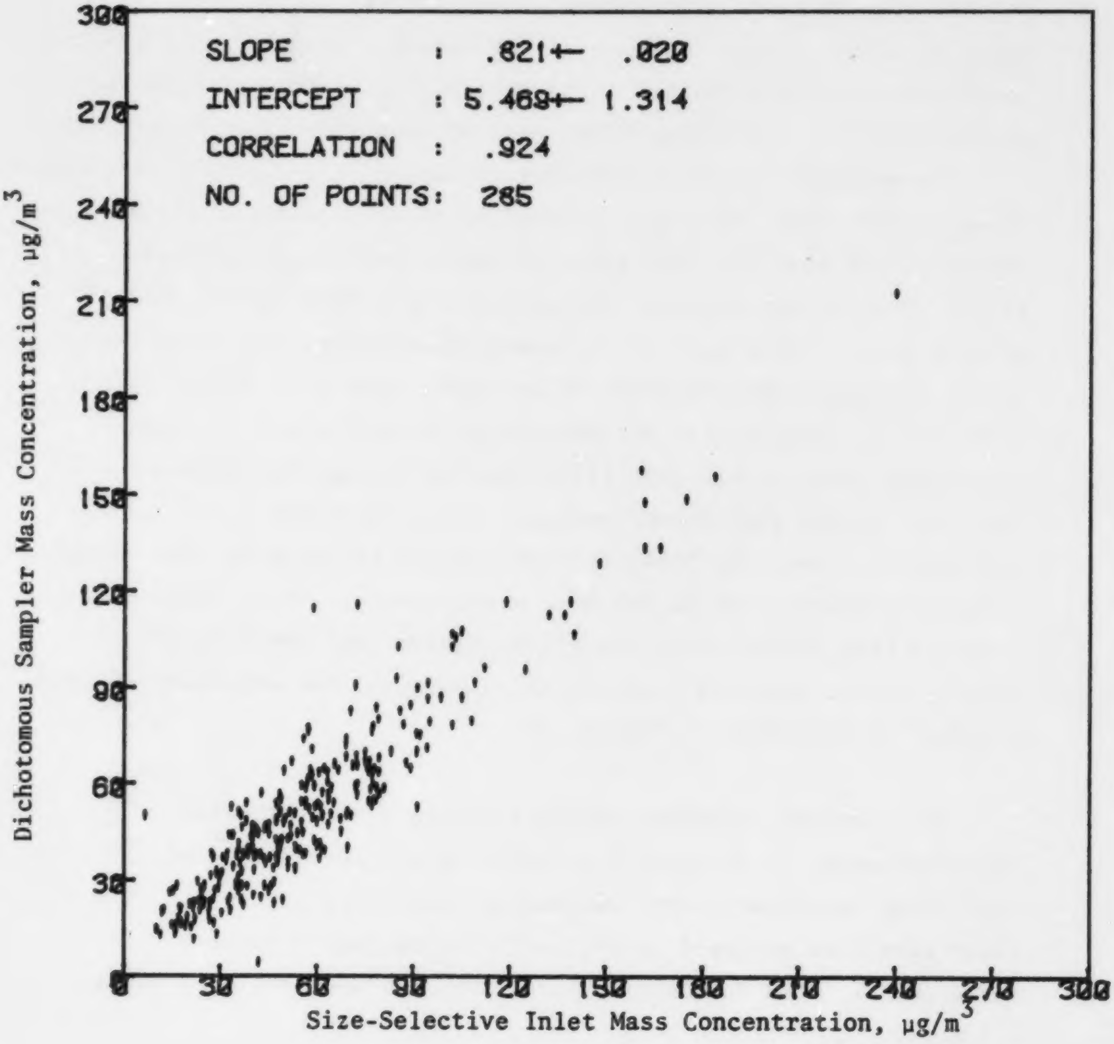


Figure 2.5.1 Scatterplot of Simultaneous Measurements of Particulate Matter with the HIVOL Size-Selective Inlet and the Dichotomous Sampler.

- Present wind tunnel testing of inlets provides useful comparisons of collection effectiveness. It is not certain that all such tests are equivalent. Standardized methods of evaluating collection effectiveness and efficiencies should be devised and applied to all samplers used for evaluating compliance with a standard. These methods might include wind tunnel measurements, sampling of standard aerosol size distributions, and simultaneous ambient sampling with established inlets.

- Inlets with 10 um 50% cut-sizes can be expected to collect between 80 and 90% of the mass collected with the present dichotomous and HIVOL size-selective inlets.

- HIVOL(SSI) and TOTAL inlets sample equivalent mass concentrations within 5% of each other under typical situations. However, under low or high wind speeds, in particle size distributions with much coarse material, or when interferences are present in one or both of the samplers, this equivalency degrades.

- The integration of the product of particle size distribution and collection effectiveness provides useful information on the average relative mass collection efficiencies of different samplers. Results of this model agree with average ratios determined from ambient measurements. These average ratios show substantial variability and a knowledge of the ambient particle size distribution and wind speed during ambient sampling is required to truly test the model.

CHAPTER 3

THE INHALABLE PARTICULATE MATTER SAMPLING NETWORK MEASUREMENT PROCESS

This chapter briefly summarizes the measurement of suspended particulate matter in the Inhalable Particulate (IP) Network. In later chapters, reference will be made to the information on sampler siting, sampling and analysis procedures, data validation and measurement precision presented in this chapter. Much of this information is included as a reference for future as well as present uses of IP Network data because it is not easily available elsewhere.

3.1 Sampler Locations and Site Descriptions

Pollutant concentrations and the causes of those concentrations vary over many geographical scales. A monitoring network design is expected to define the geographic scale over which pollutants are to be measured in accordance with the purposes for which measurements are being made and samplers must be placed in locations that are not influenced by pollutant sources which are significant contributors on a smaller scale. Table 3.1.1 shows the types of scales and the nominal separation of samplers required to represent those scales.

TABLE 3.1.1
STUDY SCALES
(*Federal Register*, 1979)

Study Scale	Nominal Sampler Separation (km)
Global	1,000
Regional	100
Urban	10
Neighborhood	1
Middle	.1
Micro	.01

The IP Network was designed primarily to characterize urban-scale concentrations of suspended particulate matter, since the attainment of air quality standards is evaluated over this scale.

However, several of the sampling sites can be termed representative of regional or neighborhood scales. Samplers are located in widely separated non-urban areas for regional representation and one study was performed to assess concentration and source contribution variations over the neighborhood scale in an industrial area. Plans are underway to complete a middle-scale study near a heavily traveled roadway.

Appropriate sampler siting is paramount when the measurements made by that sampler are to be used to interpolate the concentrations between samplers. Therefore, descriptions of the sampling sites in terms of the various geographic study scales are essential to an understanding of the accuracy with which they represent the concentrations within that scale. As yet, no simple model has been developed to place accuracy and precision estimates due to sampler siting on measurements taken at a particular site. The site descriptions must be used *a posteriori* to offer possible explanations for measurements which do not agree with expectations for a certain study scale. Most sampling sites in the IP Network follow the siting criteria devised by Ludwig et al (1977) for siting Total Suspended Particulate Matter (TSP) monitors. Though these criteria are meant to alleviate influences of local sources, practical considerations often prevent meeting them in their entirety.

Figure 3.1.1 shows the geographical distribution of the areas sampled while Table A.1 of Appendix A lists and describes the individual sampling sites within each area. The first column of Table A.1 contains a site mnemonic; the first two letters identify the state, the second two letters identify the city or town, the third letter refers to the site within the city or town, and the final two numbers define the type of sampling site. These two numbers refer to the sampling site type as defined in the first part of Table 3.1.2 after Trijonis (1980). The first number represents a regional classification of the general area surrounding the sampling site within approximately a 10 km radius, and consists of urban, suburban

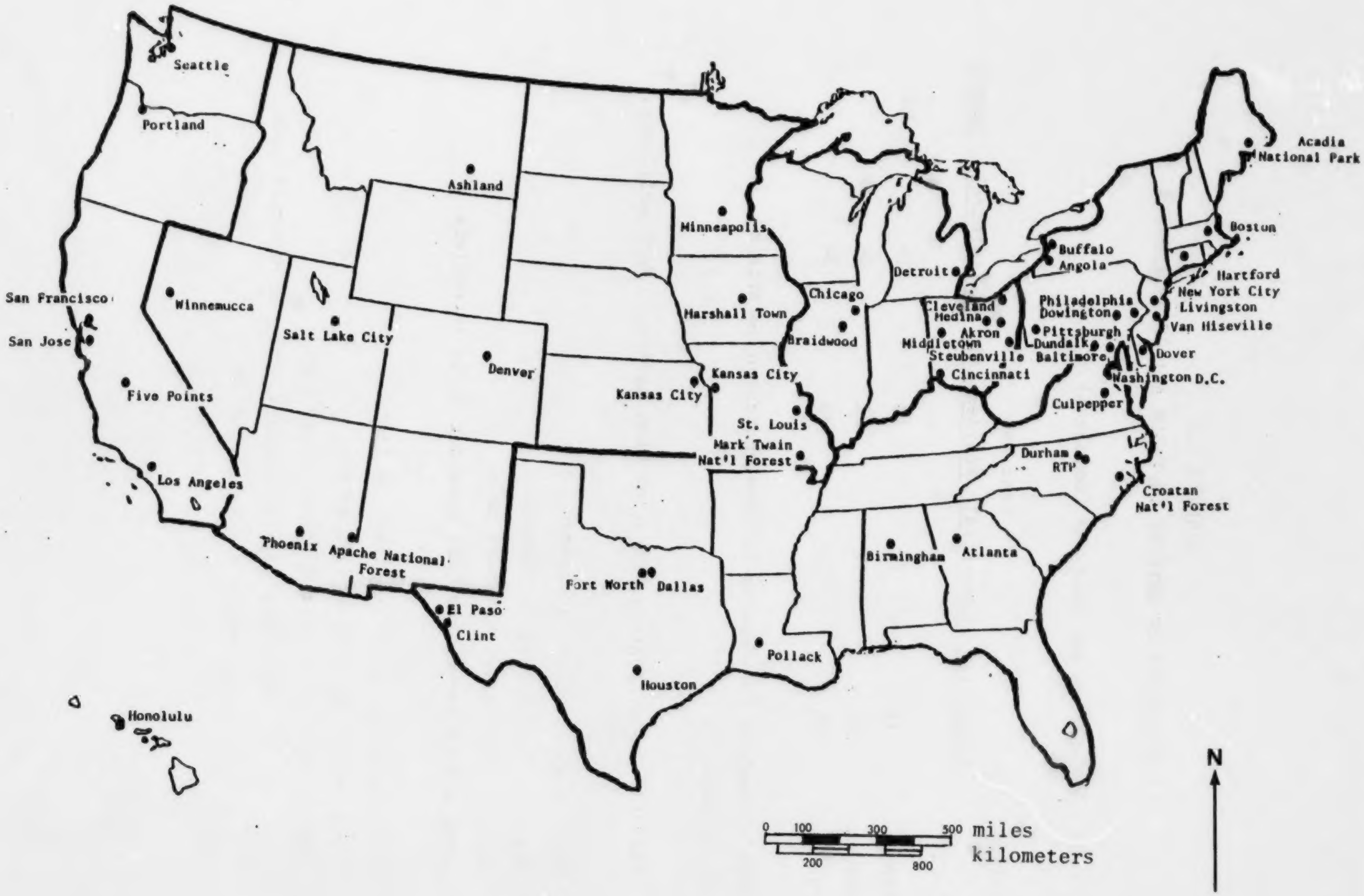

Seattle
Portland
San Francisco
San Jose
Winnemucca
Five Points
Los Angeles
Honolulu
Ashland
Salt Lake City
Phoenix
Apache National Forest
Denver
El Paso
Clint
Fort Worth
Dallas
Houston
Minneapolis
Marshall Town
Kansas City
Kansas City
St. Louis
Mark Twain Nat'l Forest
Pollack
Chicago
Braidwood
Detroit
Cleveland
Medina
Akron
Middletown
Steubenville
Cincinnati
Birmingham
Atlanta
Buffalo
Angola
Philadelphia
Dowington
Pittsburgh
Dundalk
Baltimore
Washington D.C.
Culpepper
Durham
RTP
Croatan Nat'l Forest
Dover
Van Hiseville
Livingston
New York City
Hartford
Boston
Acadia National Park
N
0
100
300
500
miles
200
800
kilometers

Figure 3.1.1 Locations of Sampling Areas in the IP Sampling Network

TABLE 3.1.2

DESCRIPTION OF ENTRIES IN TABLE A.1 OF APPENDIX A

1. Code for Location and Land Use (Column 1)

Location	Land Use				
	Industrial	Commercial	Residential	Agricultural	Remote
Urban	11	12	13	14	15
Suburban	21	22	23	24	25
Rural	31	32	33	34	35

A pair of numbers followed by "?" designates an uncertain classification.

2. Code for microinventory, Local or NAMS hardcopy, NAMS soft copy.

"*" means a site survey is planned.
"0" means no site survey is planned.
"1" means a site survey has been made.
"2" means a site survey has been made but it is incomplete.

3. Site Elevation above sea level in feet.
4. Probe height above ground in meters.
5. SAROAD code: First two digits - state code
   Next four digits - county, city or district code
   Last three digits - Site ID

and rural descriptors. The urban areas are characterized by closely spaced and heavily traveled highways, closely spaced single and multiple family dwellings, concentrated commercial establishments, and population densities of greater than 2,000 people/mi^2 or more. The suburban areas contain a small number of heavily traveled highways (usually an Interstate beltway, spur or connector), a large number of access roads, widely spaced, single family dwellings, widely separated shopping centers and population densities of the order of 2,000 people/mi^2. A rural area is characterized by few roads, scarcely traveled, dwellings separated by 1 km, open or forested areas and population densities less than 500 people/mi^2.

The second digit of the site descriptor refers to the types of land uses within approximately a 1 km radius of the sampling site. An industrial area contains one large or several moderately sized manufacturing facilities which commonly emit some form of air pollutant. A commercial area contains stores, parking lots and office buildings. A residential area consists primarily of dwellings, an agricultural area of fields, and a remote area of mountains, forests or meadows.

These classifications were given on the basis of site surveys if they were available. In the absence of site surveys, the classification assigned to a site in the Directory of Air Quality Monitoring Sites (USEPA, 1978a) was adapted to the previously described scheme (the classification in this directory is slightly different from the one presented here). Three types of site survey were used, and their existence for a particular sampling site is indicated by a code from the second section of Table 3.1.2 in columns 3, 4 or 5 of Table A.1 of Appendix A.

The most detailed site survey is the microinvetory developed by Pace (1979). This survey includes a detailed map of the area within 1/2 km of the sampling site noting roads, traffic counts, open fields, storage piles, and any visible emissions. Major point and area sources are identified within a 1.5 km radius of the site and major point sources are plotted within 8 km of the site. Estimated emission rates are assigned to each source and summed over a set of predefined sectors. Photographs in each of the cardinal directions are included. Sampling configuration (probe height, equipment, location, etc.) is also described. Microinventories were supplied by the EPA Office of Air Quality Planning and Standards (OAQPS) for the thirteen sites indicated in Table A.1 of Appendix A.

Several of the sites have been designated as National Air Monitoring System (NAMS) sampling sites. One of the requirements of a NAMS site is that it be subjected to a NAMS hard-copy site survey. This survey includes the 1/2 km map, identification of point and area sources, optional photographs, and configuration description, but it contains no estimates of relative emission rates. These hard-copy surveys were performed in Buffalo, NY and Philadelphia, PA as part of this project. Others were supplied by OAQPS. Surveys for Phoenix, AZ were taken from Richard and Tan (1977) and for El Paso, TX and Houston, TX from Price et al (1977).

The assignment of a two digit site-classification code was made by the authors of this report based on their review of the existing information. Table 3.1.3 summarizes the environs in the vicinity of each site which was identified by the survey and used to assign a site-type classification. This table provides a more detailed description to supplement the two digit codes.

A NAMS soft-copy survey, the existence of which is noted in column 5, is a computer generated listing of site coordinates, configuration and classification according to the Directory of Air Quality Monitoring Sites (USEPA, 1978a) criteria. The presence of nearby roadways or industries is often, but not always, noted on the survey. The site-type classifications from the soft-copy survey and the Directory are less accurate than those derived from the more extensive surveys because they lack detailed descriptions of the local environments. Of the 108 sites listed in Table A.1 of Appendix A, 42 presently have hard-copy surveys or microinventories and 27 are meant to have surveys taken in the near future. These detailed surveys of the sampling environment are necessary to understand the types of sources which may be contributing to the suspended particulate matter

TABLE 3.1.3

SITE SURVEY SUMMARY

Site ID	Site Name	Classification	Site Description	Site Survey Reference
ALBIA	S. Birmingham, AL	Urban - Commercial	Located 11 m from ground on roof of a three story building. Paved, curbed roads in all directions within 1/4 km from site. Heavy traffic. Point sources include iron and steel foundaries to northeast (~3 to 8 km) and blast furnaces to north and northwest (~3 to 8 km) from receptor.	Micro Invent.
ALBID	Mt. Brook, AL	Suburban - Residential	Located 3 m from ground on roof of shed. Paved, curbed roads south, west and north from site. Moderate traffic. No large point sources near receptor.	Micro Invent.
ALBIE	Tarrant City, AL	Suburban - Industrial	Receptor was moved in 1977 from 2 m to 5 m from ground. Clean, paved, curbed roads south (~1 1/2 km), west (~1 1/2 km) and east (1.6 km) from site. Heavy traffic. Unpaved parking lot 1/4 km away. Iron and steel foundaries to east (~3 km), blast furnaces at southeast (~3 km), and mineral products north and northwest (~3 km) from receptor.	Micro Invent.
AZPHA	Carefree	Rural - Agricultural	Located 1.5 m above ground level. Unpaved noncurbed roads southwest (~1/4 km) and airport runway northwest (~1/4 km) of the site. There are limited aircraft activities and light traffic around. Fugitive dust and open desert characterize the area. No significant point sources were identified near receptor.	Hardcopy (HC)
AZPHC	Phoenix, AZ	Suburban - Residential	Located 4 m from ground on roof of building. There are nearby paved roads south and northwest (~1/4 km) of the site. East of the site is a gravel and dirt alleyway with unpaved parking lots nearby. Fugitive dust from vehicular activity and by wind action. No significant point sources near receptor.	HC
CALAA	Azuza, CA	Suburban - Residential	Located 5 m from ground on roof of a building. Paved, noncurbed road. Light travel. No large point sources near receptor.	HC
CALAB	W. Los Angeles, CA	Suburban - Commercial	Located 6 m from ground on building. Paved, noncurbed roads in all directions (~1/4 km) of site. Moderate traffic. No information on point sources available.	HC

TABLE 3.1.3 (Continued)

Site ID	Site Name	Classification	Site Description	Site Survey Reference
CALAC	Pasadena, CA	Suburban - Residential	Located 6 m from ground on roof of building. Several paved roads in all directions (~1/2 km) of site. Heavy traffic. No information on point sources available.	HC
CALAD	Rubidoox, CA	Suburban - Residential	Located 7 m from ground on top of building. Trailer park 1/4 km away. Light traffic. Paved, noncurbed road close by. No large point sources nearby.	HC
CASFA	Livermore, CA	Suburban - Residential	Located 8 m from ground on top of building. Two paved roads within 1/4 km. Heavy traffic. No information on point sources available.	HC
CASFB	Richmond, CA	Suburban - Commercial	Located 9 m from ground on roof of building. Several paved roads within 1/4 km from site. Moderate to heavy traffic. No information on point sources available.	HC
CASFC	San Francisco, CA	Urban - Industrial	Located 9 m from ground on roof of building. Two paved roads within 1/4 km of site. Moderate traffic. No information on point sources available.	HC
CASJA	San Jose, CA	Urban - Commercial	Located 4 m from ground on roof of building. Three paved roads within 1/4 km. Parking lot close by. No information on point sources available.	HC
CODEA	Downtown, CO	Urban - Commercial	Located 14 m from ground. Paved, curbed roads at north, east (~4 km) and south (~6 km) of the site. Dust collects near edges & roads. Heavy traffic. No significant point sources near receptor.	HC
CODEB	Gates Rubber Co., CO	Urban - Industrial	Located 11 m from ground on top of building. Paved curbed roads west, east (~4 km) and north (~6 km). Heavy traffic. No significant point sources near receptor.	HC
KSKAA	Fairfax Fire Station, KS	Urban - Industrial	Located 3 m from roof of fire station. Paved road close by. Unpaved parking lots within 1/2 km of receptor, adjacent to Municipal Airport. Heavy traffic. Several large point sources within 2 km of recepter. (No detailed information on point sources available.)	Micro Invent & HC
MOSLA	Trailer, MO	Suburban - Commercial	Located 3 m from ground. Moderate Traffic. No large point sources near receptor.	HC

TABLE 3.1.3 (Continued)

Site ID	Site Name	Classification	Site Description	Site Survey Reference
MOSLB	Fire Station, MO	Urban - Residential	Located 10 m from ground, on roof of fire station. Paved curbed roads with unpaved parking lots around. Heavy traffic on dense residential area. Point sources include quarry & electric company southeast (~4 to 6 km) from receptor.	Micro Invent.
NYBUA	P. S. #26, NY	Urban - Industrial	Located 6 m from ground on a roof of a three story school building. Paved curbed roads east (~1/2 km), west (~1/10 km) and north (~1/20 km). Moderately traveled roads. Point sources include steel & iron company west and southeast (~3 to 5 km) from receptor.	HC
NYBUB	Big Sister Sewage Treatment Plant, NY	Suburban - Residential	Located 2 m from ground on top of a one story building. Paved curbed road at west (~1/2 km), south (~1 km), and east (~1 1/2 km) from the site. Light traffic with paved parking lots awest (~1/4 km) of site. No significant point sources near receptor.	HC
NYBUC	P. S. #28, NY	Urban - Industrial	Located 8 m from ground on roof of a four story building. Paved noncurbed roads at north and northeast (~1/4 km) from site. Heavily traveled roads within 5 km in all directions. Point sources include steel and iron company west (~1/4 to 3/4 km), coke production company northwest(~2 km), and a refinery north (~2 to 3 km) of the site.	HC
NYBUD	Wilmuth Pump Station, NY	Urban - Industrial	Located 2 m from ground on a one story building. Paved curbed roads within 1/4 km in all directions. Not much traffic nearby. Point sources include a steel and iron company southwest, west & northwest (~1/4 km) from site. Furnace company located north & northwest (~2 to 3 km) of receptor.	HC
ORPOA	Sauvie Island, OR	Rural - Agricultural	Receptor located 4 km from ground on roof of fire trailer. Unpaved road at northeast (~1/4 km) of the site. Light traffic. Fugitive dust characterize the area. No large point sources near receptor.	Micro Invent.
ORPOB	Central Fire Station, OR	Urban - Commercial	Receptor located 15 m from ground on roof of fire station. Paved curbed road in all directions. Heavy traffic. One acre construction 1/4 km away. No large point sources nearby.	Micro Invent.
PAPIA	Imperial High School, PA	Suburban - Residential	Receptor located 11 m from ground on roof of school. Paved curbed driveway (~1/10 km) and paved curbed roads south (~3/4 km) and directly east of site. Light traffic. No significant point sources near receptor.	Micro Invent.

TABLE 3.1.3 (Continued)

Site ID	Site Name	Classification	Site Description	Site Survey Reference
PAPHA	500 S. Broad, PA	Urban - Commercial	Located 12 m from ground on roof of a building. Paved curbed roads in all directions (~1/2 km) from site. Heavy traffic. No large point sources near receptor.	Micro Invent.
PAPHB	Allegheny, PA	Urban - Industrial	Located 6 m up from ground on Air Management Services' trailer. Paved curbed roadways northwest (~1/10 km) northeast (~1/10 km) of site. Unpaved road at west (~1/4 km) of the site. Heavy traffic. Point sources include iron and metal scrap yard northwest (~3/4 km), grain loading facility southwest (~1/4 km), and mineral handling southwest to south (~1/2 km) of receptor.	Micro Invent.
PAPHC	Belmont Water Treatment, PA	Suburban - Residential	Located 5 m from ground. Paved non-curbed roads south (~2 km) and east (~4 km) of the site. Light traffic nearby. No large point sources near the receptor.	Micro Invent.
PAPHD	S.E. Sewage Plant, PA	Urban - Industrial	Located 5 m from ground on concrete slab. Unpaved roads south and southeast of site (~1/4 km). Also open ground & lagoon construction at sewage plant east (~1/4 km). Heavy traffic on paved roads southwest and northwest (~1/2 km) from site. No large point sources near receptor, but lots of construction nearby during the sampling period.	Micro Invent.
PAPHE	N.E. Airport, PA	Suburban - Residential	Located 5 m from ground on Air Management Services' trailer. Gravel road south (~1/4 km) of the site. Helicopter landing area southeast (~1/4 km) of site. Moderate traffic with paved parking lot south (1/4 km) of the site. No large point sources near receptor.	Micro Invent.
PAPHI	St. John's Church, PA	Urban - Industrial	Located 5 m from ground on top of church garage. Clean curbed paved roads around in all directions (~1/4 km) from site. Paved parking lot northeast (~1/4 km) of site. Light traffic. Point source includes metal company (~1/2 km) northwest of receptor.	HC
PAPHJ	Pilot Freight Motor Co., PA	Urban - Industrial	Located 8 m from ground, on top of Pilot Freight Motor Co. Paved, curbed roads northeast (~1/10 km) to northwest (~1/4 km) of site. Paved parking lot south (~1/4 km) of site . Point sources include a truck firm northwest (~10 km) right next to the site; copper scrap yard east (~1/4 km), coke oven northeast (~1/2 km); and metals company northwest (~1/4 km) of receptor.	HC

TABLE 3.1.3 (Continued)

Site ID	Site Name	Classification	Site Description	Site Survey Reference
PAPHK	NEWPC, PA	Urban - Industrial	Located 5 m from ground on top of treatment plant. Dirt road east (~1/3 km) of the site. Paved curbed roads in all directions (~1/4 km). Moderate traffic. I-95 northwest (~3/4 km) of the site. Fugitive dust from exposed areas. Reconstruction of sewage plant while sampling. Point sources include copper smelting and metals company south and southwest(~1/4 km) of the receptor.	HC
PAPHL	T&A Pet, PA	Urban - Industrial	Located 5 m from ground on top of garage. Paved, noncurbed, clean roads southeast (~1/10 km) of the site. Moderate traffic. Point sources include grain loading, mineral handling south (~1 km), and metals & chemical companies north & northwest of the receptor.	HC
PAPHM	NE Transfer, PA	Urban - Industrial	Located 10 m from ground on top of NE Transfer building. Paved, curbed roads northwest (~1 1/2 km) to northwest (~1/4 km) of the site. One unpaved road located north (~1/2 km) of the site. Moderate traffic. Truck loading facility at site. Point sources include a copper smelting company northwest (~1/2 km) and an electric company east (~1/4 km) of the receptor.	HC
PAPHN	Bridesburg Rec. Ctr., PA	Urban - Industrial	Located 5 m from ground, on top of Bridesburgh Recreation Center building. Paved, noncurbed roads in all directions (~1/4 km) of the site. Open play ground at east (~1/2 km) of the site. Light traffic. Fugitive dust from exposed area. Point sources include a coke company south (~1/4 km) and a chemical company northeast and northwest (~2 to 3 km) of the receptor.	HC
TXHOB	CAMS 1, TX	Urban-Industrial	Located 6 m from ground, on top of school building. Unpaved roads and unpaved parking lots located directly north (~16 km) and south (~8 km). Heavy traffic. Point sources include lime production southeast (~8 km), coke ovens southeast (~8 km) and grain handling southeast (~16 km) of the receptor.	HC
TXELA	El Paso, TX	Urban - Commercial	Located 7 m from ground, on top of Health Dept. building. Paved roads north (~1/2 km) and east (~8 km) of the site. Moderate traffic. Fugitive dust characterizes the area. Point sources include copper smelting northwest (~5 km), lead blast furnace northwest (~5 km) and fluid catalytic crackers northeast (~8 km) from the receptor.	HC

concentrations at each site. Surveys of the remaining 39 sites should be planned before the termination of the IP monitoring program to complete the record.

Table A.1 of Appendix A contains other information about the sites. The elevation above sea level, the EPA SAROAD identifier, the UTM coordinates, and the sampler height above ground level are in columns 6 to 10. Columns 11 and 12 present the inclusive sampling dates from which measurements were drawn for the majority of the work in this report. Because this amount of data was insufficient for some purposes, data which became available later in the study were added to this set. This will be noted when the data are presented. The final three columns denote the presence (1) or absence (0) of HIVOL, HIVOL(SSI), and dichotomous samples, respectively, for the designated period.

3.2 Filter Media

In recent years certain filter media have been found to bias the measurement of suspended particulate matter. This section examines the extent of those biases in IP filter media. Special attention is given to the change of SSI and HIVOL media between 1979 and 1980 and the effect this change could have on ion mass concentration measurements.

To adequately quantify ambient mass concentrations of suspended particulate matter, the filter media selected for sampling should have collection efficiencies greater than 95 to 99% for all particle sizes, should have tensile and mechanical strength to withstand sampling, analysis and transport, should present a low enough flow resistance to its sampler that an adequate aerosol deposit can be obtained, and should be free of interferences and variable blank concentrations that might affect measurements to be made on the aerosol deposit.

The fiber filters used for HIVOL and SSI sampling and the Teflon filters used for dichotomous sampling generally meet all of the criteria except for that of blank levels and interferences.

Stevens et al (1978) have evaluated the Ghia Teflon filters for blanks and interferences and found them generally acceptable for the IP Network measurements except for the possible loss of nitrate. The glass fiber filters are another story. Two types of fiber filter were used in the IP Network; HIVOL and SSI samples in 1979 were taken on Microquartz fiber filters (Walling, 1981) while those after 1980 were taken on Schleicher and Schuell (S&S) HV-1 EPA grade glass fiber filters with an organic binder (Rodes, 1981).

Sixteen samples of blank quartz filters and two samples of blank S&S filters of the same type which were used in the IP Network were submitted to automated colorimetric and carbon analysis as described in Section 3.3. The blank values for sulfate and nitrate concentrations for Microquartz filters used during 1979 were .08 and .03 ug/cm^2 (equivalent to .02 and .01 ug/m^3 if 1600 m^3 are sampled) and .34 and .05 ug/cm^2 for S&S filters (Clark, 1981, Walling, 1981). The total carbon and total organic carbon blanks for quartz filters were measured by the authors of this report to be 7.5 ± 3.5 and 5.2 ± 2.2 ug/cm^2 (1.9 ± .9 and 1.3 ± .6 ug/m^3). The total carbon and organic carbon measured on two S&S filters were 186 ± 23 and 118 ± 10 ug/cm^2 (47 ± 6 and 30 ± 2.5 ug/m^3), respectively.

While the sulfate and nitrate blanks of both filters are lower than most ambient levels, the high levels and variability of the carbon blanks make the S&S filter unacceptable for carbon analysis. The quartz filter carbon blank is variable, but it is lower than most ambient carbon levels. The quartz blank could probably be reduced by pre-firing the filter before initial weighing. Because the organic binder is an integral part of the the S&S filter, pre-firing might damage it.

Also of great concern is the possibility of artifact formation of sulfate and nitrate; not only would these artifacts bias sulfate and nitrate concentration measurements, they would also bias the mass measurements. There is substantial evidence for sulfate and nitrate artifacts on commonly used HIVOL filter media. It has been shown that filters can adsorb SO_2 which is oxidized to $SO_4^=$. Thus sulfate measurements on the filter represent both ambient sulfate and artifact sulfate. The factors affecting artifact sulfate formation have been reported to be filter alkalinity, SO_2 concentration, humidity, temperature, and volume of air pulled through the filter (Coutant, 1977, Pierson et al, 1980). Coutant estimated the range of normal sampling error due to SO_2 adsorption on a basic filter (like glass fiber) to be between .3 to 3 ug/m^3. Shaw et al (1981) found that mass and sulfate collected by the SSI were higher than simultaneous TOTAL mass and sulfate measurements. They hypothesized that the extra mass was due primarily to sulfate artifact and, to a lesser extent, to the combination of the positive and negative nitrate artifacts.

Nitrate sampling errors are primarily due to gaseous nitric acid in the atmosphere and have been shown to be substantial for glass fiber filters (Spicer and Schumacher, 1977; Appel et al, 1981b; Meserole et al, 1979). The use of an inert filter, such as Teflon, to minimize the positive nitrate interference is prone to a negative interference resulting from the volatilization of HNO_3 (Appel et al, 1981b, Pierson et al, 1980).

Filter media may not be the only factor influencing the reported nitrate concentrations measured with IP Network samplers, however. In a field test of four samplers in California, Wendt and Torre (1981) found that the particulate nitrate collected by the SSI averaged 3.8 ug/m^3 less than that of the corresponding HIVOL samples. It was hypothesized that the observed difference was due to loss of gaseous nitric acid on the aluminum surface of the size-selective inlet. Analysis of washings of the aluminum surface accounted for 92% of the missing nitrate (or HNO_3 vapor). They found no difference in sulfate concentrations between the SSI and HIVOL samples. Appel (1981a) is currently investigating the potential of artifact formation for different filter media used by EPA.

The IP Network measurements offer the possibility of evaluating the difference in artifact formation properties of IP Network filters. Because the data are sparse and preliminary, this evaluation must be considered illustrative rather than definitive. It does provide a motivation for further study of IP Network filter mdeia. It also raises some cautions about the interpretation of sulfate, nitrate and even mass measurements made in the IP Network. For this report, the IP mass concentration data were separated into two subsets, 1979 (quartz) and 1980 (S&S), to evaluate the changes which might have occurred because of the switch in the filter medium. The geometric and arithmetic averages, standard deviations, and number of samples for the ambient aerosol concentrations as measured by HIVOL, SSI, and dichotomous samplers are given in Table 3.2.1. The cumulative frequency distributions for all measurements at all sites were also plotted to see if any changes were evident before and after 1980; these plots showed the 1980 distribution shifted several ug/m^3 higher than the 1979 distribution for HIVOL and SSI, but not for 1979 and 1980 TOTAL mass concentrations.

As seen in the Table 3.2.1, the COARSE average as sampled by the dichotomous sampler remained the same from the 1979 to the 1980 subset, while the FINE average decreased. This is reflected in the TOTAL arithmetic average which decreased from 47 to 43 ug/m^3. The HIVOL and SSI arithmetic averages increased from 70 to 71 ug/m^3 and 54 to 58 ug/m^3, respectively. Though these increases were not large, the trend was opposite that of the dichotomous sampler.

A rough estimate of the additional average mass collected by the S&S filters over the quartz filters is tabulated in Table 3.2.2. The assumption is that if the quartz filter had been used in 1980, the ratio of average SSI (1980) to SSI (1979) and average HIVOL (1980) to HIVOL (1979) would be the same as average TOTAL (1980) to TOTAL (1979) ratio. As seen in the Table 3.2.2, the average mass concentration measured on S&S filters seems to be higher than that measured on quartz filters by about 7 ug/m^3 for both SSI and HIVOL. This amounts to about 11% additional mass measured for HIVOL and 17% additional mass for SSI with the use of S&S filters. The slightly larger additional mass for SSI, if it could be attributed to artifact, might be due to the lower flow rate for the SSI (Coutant, 1977) as compared to the HIVOL (the SSI flow rate is 40 cfm while the HIVOL flow rate is 50 cfm) which would make the relative increase of the SSI average mass higher than that of the HIVOL mass if the SO_2 adsorption reached saturation during the sampling period. Thus, mass measurement comparisons show that, on an average, 7 ug/m^3 of additional mass was collected in 1980 over that collected in 1979.

TABLE 3.2.1

COMPARISONS OF ARITHMETIC AND GEOMETRIC AVERAGE MASS CONCENTRATIONS FOR HIVOL, SSI, TOTAL, FINE AND COARSE TAKEN IN 1979 AND 1980

	Geometric Average (ug/m^3) and Standard Deviation				Arithmetic Average (ug/m^3) and Standard Deviation			
	1979		1980		1979		1980	
Category	Avg	Std Dev	Avg	Std Dev	Avg	Std Dev	Avg	Std Dev
HIVOL[a]	58	2	60	2	70	44	71	42
	(1,041)[c]		(1,046)		(1,041)		(1,046)	
SSI[a]	47	2	51	2	54	30	58	31
	(316)		(455)		(316)		(455)	
TOTAL[b]	40	2	37	2	47	31	43	22
	(714)		(795)		(714)		(795)	
FINE[b]	22	2	18	2	26	18	22	12
	(714)		(795)		(714)		(795)	
COARSE[b]	16	2	16	2	21	18	21	16
	(714)		(795)		(714)		(795)	

[a] Sampling done using quartz filters for 1979 subset while S&S filters were used in 1980.

[b] Dichotomous samplers employed Teflon filters throughout.

[c] Number of measurements in average.

TABLE 3.2.2

COMPARISON OF MEASURED ARITHMETIC AVERAGE CONCENTRATIONS IN 1980 ON S&S FILTERS TO THOSE PREDICTED FROM 1979 MEASUREMENTS ON QUARTZ FILTERS

	Arithmetic Average Concentrations in ug/m3	
	HIVOL	SSI
1980 Arithmetic average from S&S filter measurements	71	58
1980 Arithmetic average predicted[a] from 1979 quartz filter measurements	64	49
Difference	7	9

[a] Obtained by multiplying the 1979 averages for HIVOL and SSI by .915, the ratio of arithmetic average TOTAL in 1980 to TOTAL in 1979.

TABLE 3.2.3

COMPARISON OF 1979 and 1980 ARITHMETIC AVERAGES OF MASS CONCENTRATION RATIOS

	SSI/HIVOL		TOTAL/HIVOL		TOTAL/SSI	
	Avg	Std	Avg	Std	Avg	Std
1979 (Quartz)	.734	.124	.783	.158	1.078	.226
	(293)[a]		(578)		(86)	
1980 (S&S)	.715	.150	.668	.178	.902	.206
	(390)		(557)		(179)	

[a] Number of measurements in average.

These averages do not result from simultaneous measurements, and they could be different just because the data sets from which they were derived were different. However, one possibility is that additional mass collected by the 1980 SSI and HIVOL samples is due to a sulfate and, to a lesser extent, a nitrate artifact which occur on the S&S filters but not on the quartz filters.

The same conclusion is drawn from the comparison of 1979 and 1980 arithmetic average ratio measurements given in Table 3.2.3. These ratios are calculated from measurements made at the same site at the same time. The average ratios of TOTAL/SSI and TOTAL/HIVOL decrease by about 15% from the 1979 to the 1980 subset. This corresponds to about 7 ug/m^3 of additional mass collected, on an average, by HIVOL and SSI samplers in 1980 over that collected in 1979. The ten percent difference between the TOTAL/SSI ratios is similar to that noted in Section 2.5.

The portion of the additional 1980 mass attributable to sulfate and nitrate artifacts can be estimated by comparing the sulfate and nitrate concentrations measured on SSI, HIVOL, and TOTAL samples taken during 1979 and 1980. Once again, since the number of data points is small, this comparison cannot be considered conclusive. The 1979 scatterplots for nitrate are not included because nitrate measured on SSI was close to the lower quantifiable limit.

Figures 3.2.1 a and b are scatterplots and linear regression parameters of the TOTAL/SSI sulfate measurement from samples taken during 1979 and 1980, respectively. In 1979, the simultaneous measurements were nearly equal for all samples considered. The linear regression slope of 1.06 shows overall equivalency within experimental precisions. The data points approach zero for TOTAL and SSI measurements. In 1980, the TOTAL sulfate was considerably less than the concurrent SSI sulfate in almost all cases. The linear regression slope is .68, a considerable reduction from that calculated for 1979 measurements and well outside the bounds imposed by normal measurement precisions. The 1980 plot shows minimum sulfate concentrations of approximately 3 ug/m^3 for SSI measurements even though the TOTAL sulfate concentrations approach zero. The maximum absolute amount by which an individual SSI sulfate measurement exceeded a TOTAL measurement in 1980 was 8 ug/m^3 while it was only 3 ug/m^3 for the 1979 data.

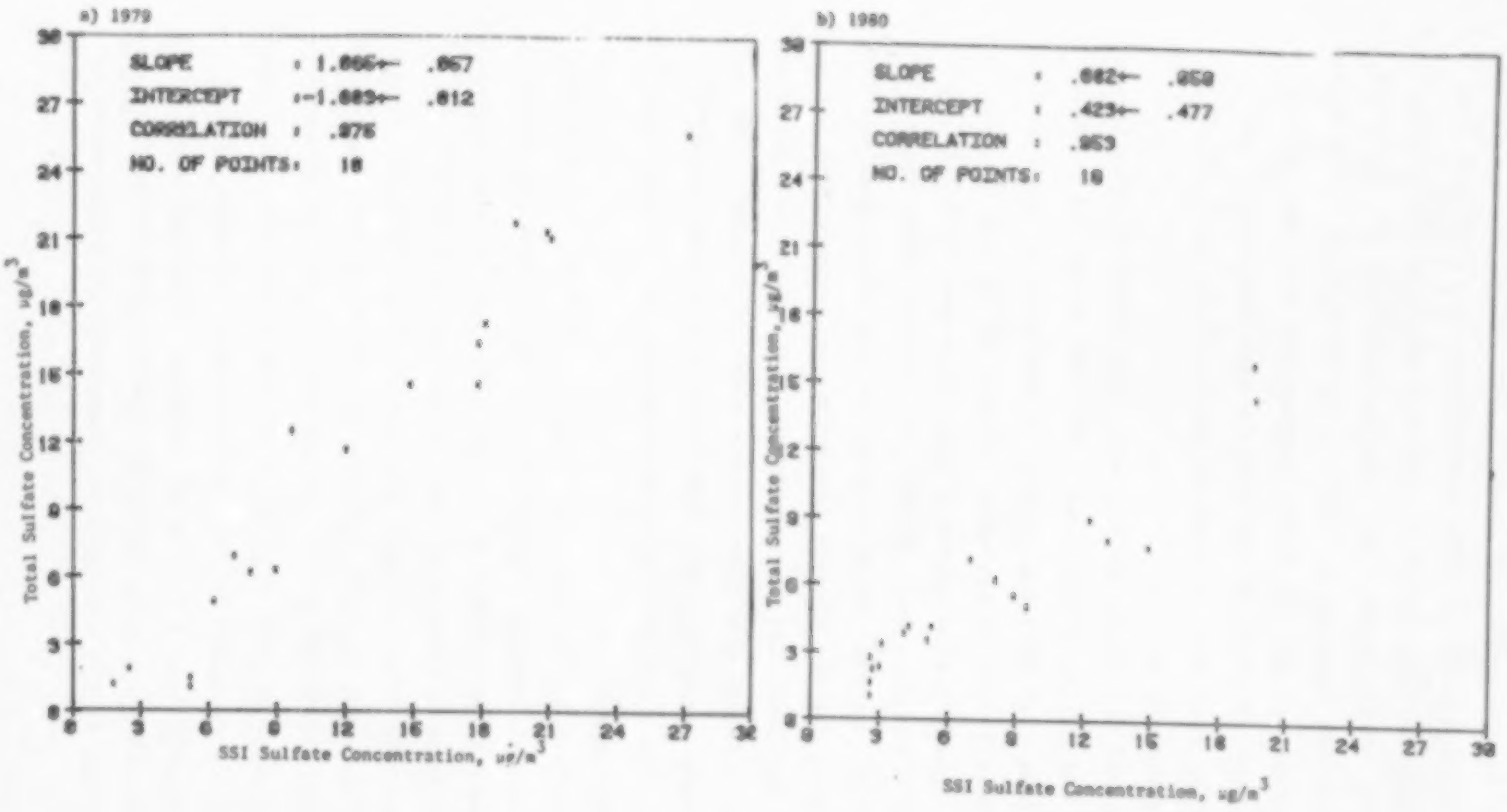


Figure 3.2.1a-b - Scatterplot of Simultaneous TOTAL and SSI Sulfate Concentrations from all IP Sampling Sites in 1979(a) and 1980(b).

Similar observations do not apply to the comparison of simultaneous HIVOL and SSI sulfate measurements for 1979 and 1980 presented in Figures 3.2.2 a and b. The two measurements during both years are nearly equal, with linear regression slopes which do not significantly differ from unity. This is to be expected when filter media for simultaneous SSI and HIVOL samples are the same, either quartz or S&S; any artifact is the same on both samples. These figures also show that most sulfate is contained in particles with diameters less than 15 um.

The TOTAL/SSI and HIVOL/SSI nitrate comparisons are plotted in Figures 3.2.3 and 3.2.4, respectively, for 1980 data; SSI nitrate measurements from 1979 were inadequate to form such a comparison for that year. There is little agreement between TOTAL and SSI measurements, though SSI is almost always in excess of TOTAL. The combination of a variable loss of nitrate from the TOTAL and a gain of nitrate on the SSI samples could account for the discrepancies. In the extreme case, one SSI nitrate concentration exceeded the corresponding TOTAL nitrate concentration by 5 ug/m^3. SSI nitrate concentrations approach a minimum on the order of 1 ug/m^3. The SSI/HIVOL nitrate comparison for 1980 exhibits the same properties as those shown by the corresponding sulfate plots; the measurements are essentially equivalent.

If the sulfate and nitrate on the Teflon filters are used to estimate the actual ambient concentrations, the linear regression lines corresponding to Figures 3.2.1 and 3.2.3 can be used to estimate the additional mass collected on S&S filters due to artifact formation. Average TOTAL sulfate and nitrate concentrations from various sampling sites are tabulated in Chapter 9 of this report and are of the order of 10 ug/m^3 for sulfate and 2 ug/m^3 for nitrate. The linear relationships of Figures 3.2.1 and 3.2.3 yield expected SSI concentrations of 14 ug/m^3 sulfate and 4.3 ug/m^3 nitrate. This amounts to approximately a 6.3 ug/m^3 increase in average mass concentrations which could be attributed to artifact formation, an amount very close to the average mass concentration differences of Table 3.2.2.

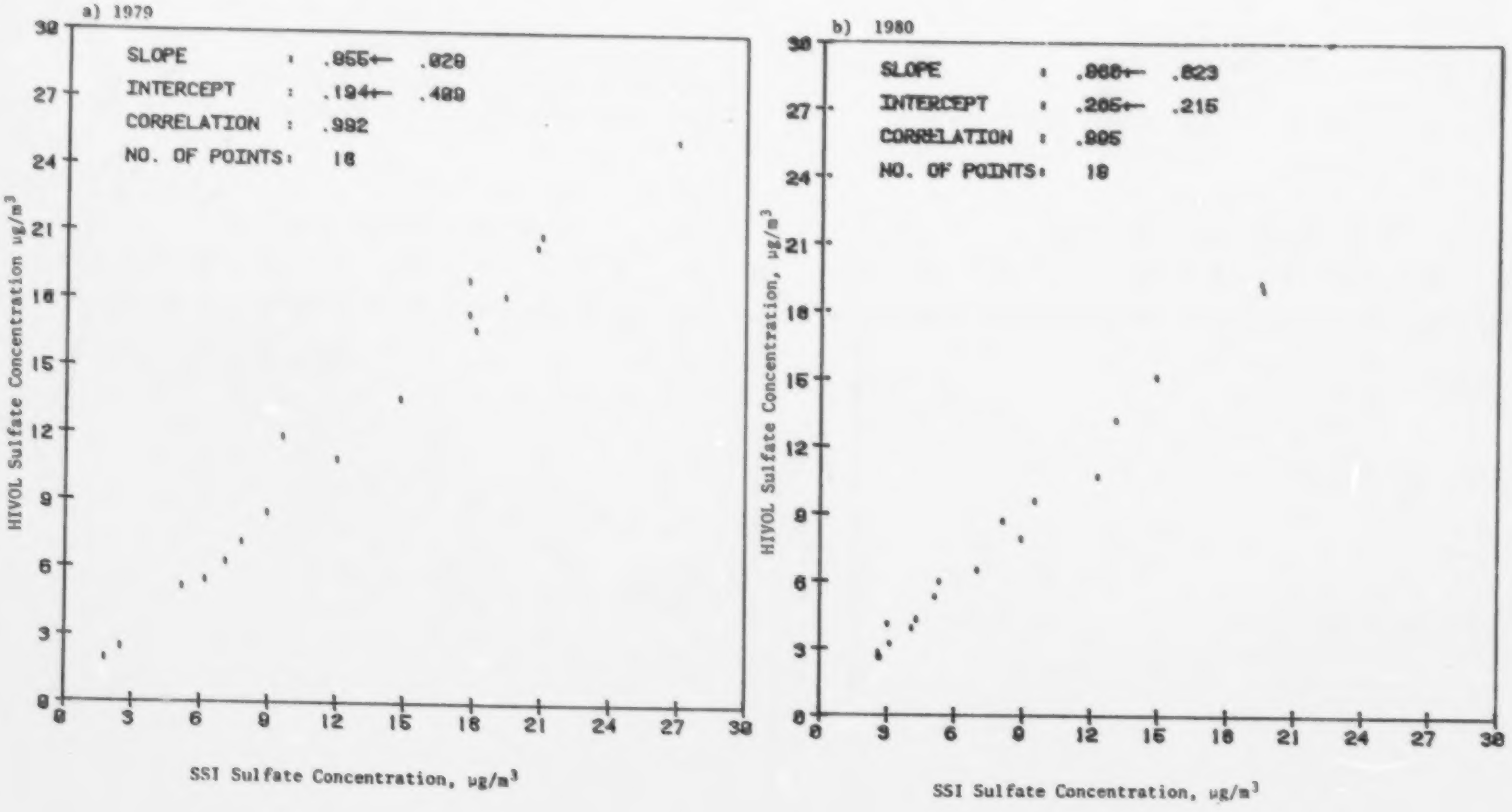


Figure 3.2.2 a-b Scatterplot of Simultaneous HIVOL and SSI Sulfate Concentrations from All IP Sampling Sites in 1979 (a) and 1980 (b).

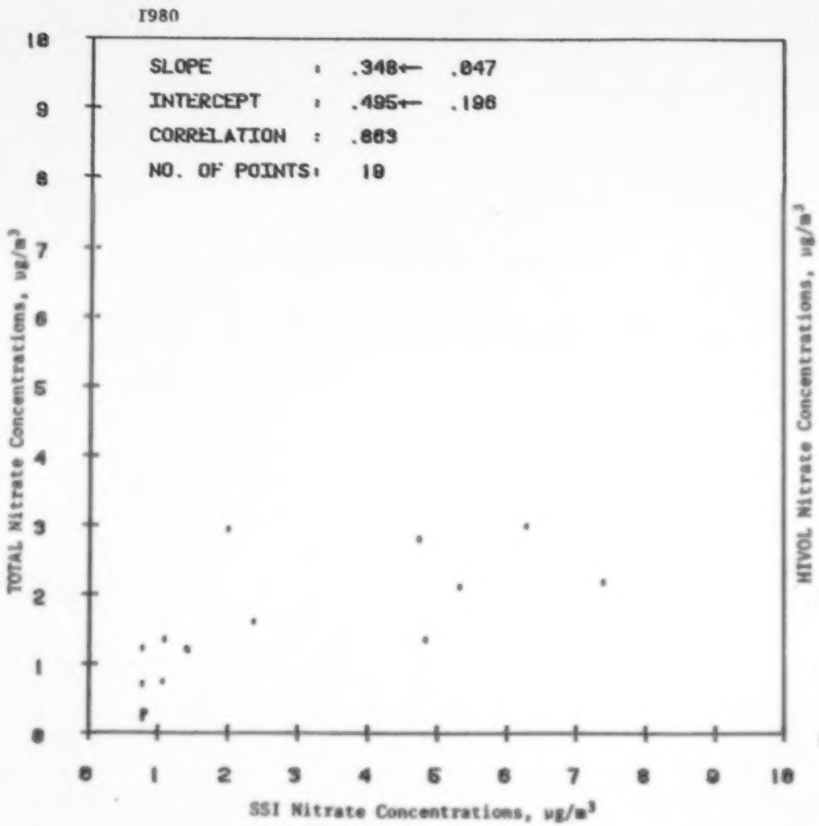


Figure 3.2.3 Scatterplot of Simultaneous TOTAL and SSI Nitrate Concentrations from all IP Sampling Sites in 1980.

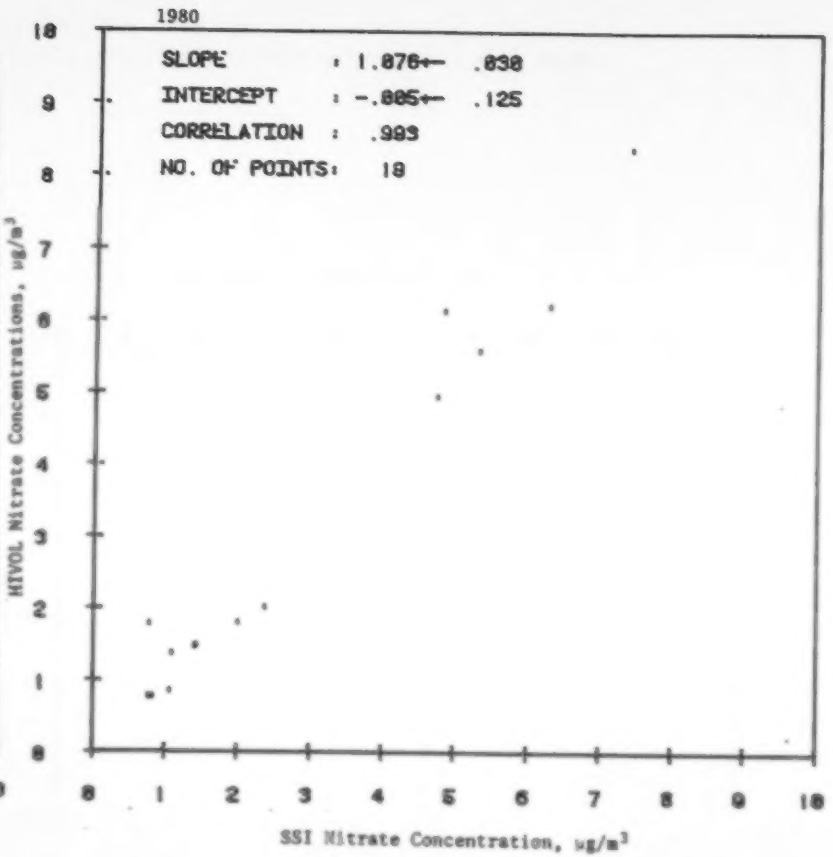


Figure 3.2.4 Scatterplot of Simultaneous HIVOL and SSI Nitrate Concentrations from all IP Sampling Sites in 1980.

It should be cautioned once again that the above observations are based on scatterplots made using 18 to 19 data points. However, all evidence points in the same direction: filter artifacts due to the use of the S&S filter for IP sites in 1980 could account for a significant part of the difference between SSI and TOTAL average mass measurements and can bias the reported sulfate and nitrate concentrations.

For a variety of reasons, EPA has changed the type and manufacturer of the filter media which are used in its ambient monitoring networks. This procedure poses serious problems to the interpretation of data. As pointed out in this section, the switch during 1980 to S&S filters resulted in possible biases of sulfate, nitrate and mass measurements. Also, S&S filters have very high and variable total carbon blank values which makes carbonaceous aerosol analysis by combustion methods impossible. Switching of filter types also limits the use of data for long term trend analysis. It is not too unusual to analyze for the first time or to reanalyze samples collected years ago. This limits the potential use of such samples.

3.3 Network Operations

Mass, elemental and ionic concentration measurements in the Total, Inhalable, and Fine Suspended Particulate Matter are produced by the IP Network Monitoring System (USEPA, 1980c). In addition to these routine analyses, several special filters were selected for optical microscopic and carbon analysis in addition to non-routine analysis for ions and elements as part of this study and separate from normal IP Network procedures. This section briefly describes the analysis procedures followed for all of these measurements and lists some of the limitations of the methods used.

The overall flow of routine tasks performed on the samples collected is summarized in Figure 3.3.1. All the samplers in the network were supplied by Environmental Protection Agency's Environmental Monitoring Systems Laboratory (EPA/EMSL) and operated by state or local agency personnel. The filters were weighed and sent to sites by EPA/EMSL in Research Triangle Park, NC. The sampling was carried out for 24 hours, midnight to midnight, every sixth day (or

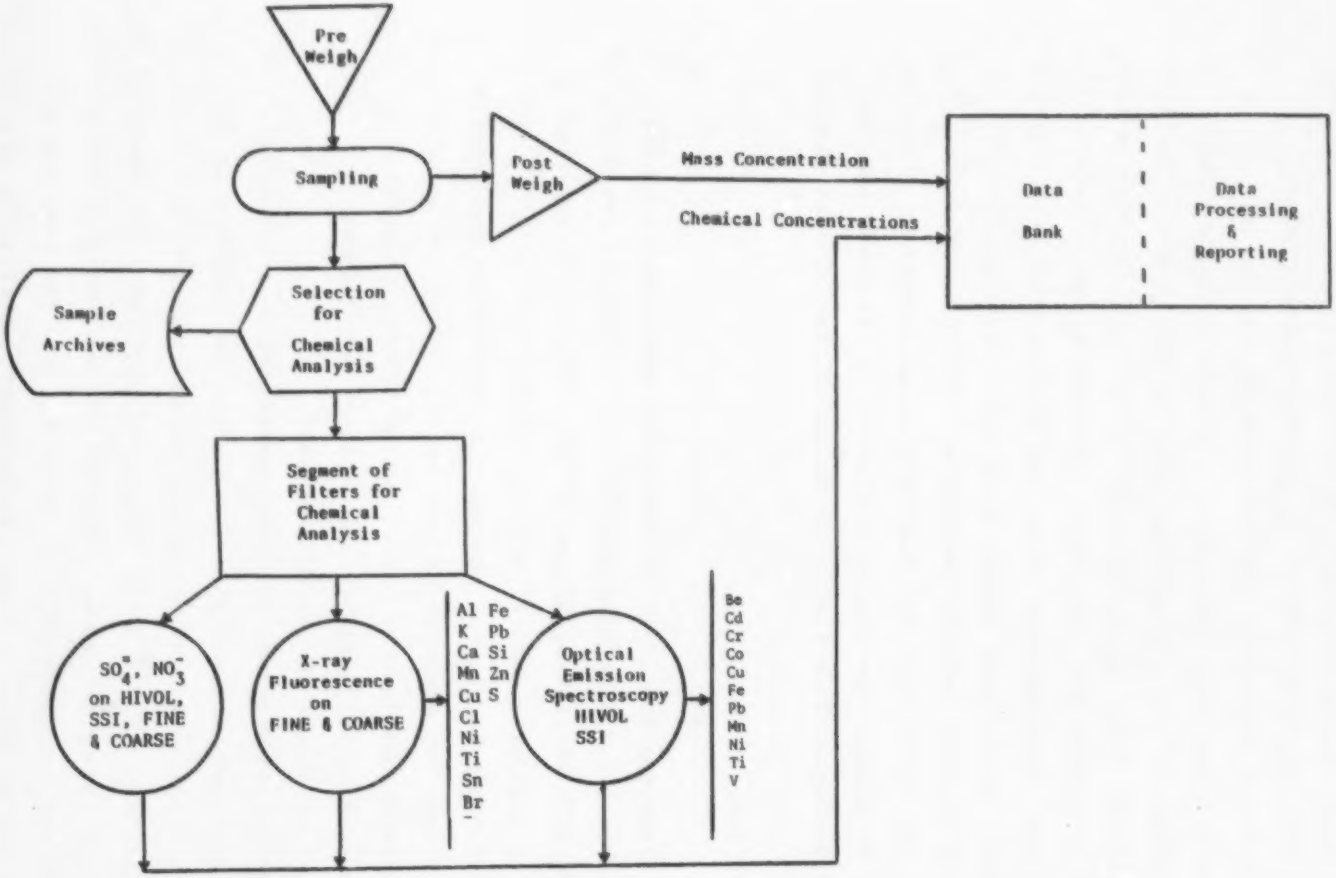

Pre Weigh
Sampling
Post Weigh
Mass Concentration
Chemical Concentrations
Data Bank
Data Processing & Reporting
Sample Archives
Selection for Chemical Analysis
Segment of Filters for Chemical Analysis
$SO_4^=$, NO_3^- on HIVOL, SSI, FINE & COARSE
X-ray Fluorescence on FINE & COARSE
Al K Ca Mn Cu Cl Ni Ti Sn Br
Fe Pb Si Zn S
Optical Emission Spectroscopy HIVOL SSI
Be Cd Cr Co Cu Fe Pb Mn Ni Ti V

Figure 3.3.1 Flow of Routine Tasks Performed in the IP Network Operations

third day in some cases). The samples were returned to EPA/EMSL for weighing and possible further analysis. Mass concentrations were calculated for all samples. Sections of a selected number of filters were submitted for chemical analysis to determine sulfate, nitrate, and a variety of elemental concentrations. Sulfate and nitrate were measured on all filters using automated colorimetry. Elemental concentrations on HIVOL and SSI filters were measured by optical emission spectroscopy and on Teflon filters by x-ray fluorescence. Ion and elemental analyses were performed on approximately 25% of all samples.

3.3.1 Filter Weighing

The HIVOL and SSI fibrous filters (8" x 10") were allowed to equilibrate for at least 24 hours in a control box where relative humidity was below 50% and temperature was between 15 to 35°C. The weighing was done using a Mettler balance with a sensitivity of .1 mg. Internal quality control was carried out by checking the zero of the balance after every fifth weighing and by requiring immediate investigation of any blank filter that weighed above or below the range of 3.5 to 5.0 g. External quality control was carried out by the reweighing of 4 filters out of each set of 100 by another technician. If all of the reweights were within 2.8 mg of the original weight for blanks and 5 mg for exposed filters, all weights were accepted. External audits by supervisory personnel were conducted at unannounced times.

The Teflon membrane filters (37 mm) used with dichotomous samplers were also equilibrated as desribed earlier and weighed using a Mettler microbalance precise to ± 1 ug. The exposed filters were reweighed on the balance on which their tared weights were obtained. The internal quality control was carried out by weighing a "standard" filter, arbitrarily selected for that purpose, at the beginning of each day. If the weight of the standard filter was not within 20 ug of the established value, a full-scale balance checkout was undertaken before regular filter weighing commenced. About 6 filters were reweighed by another technician for each balance per day. If the reweights were not within 20 ug of the original value, the difficulty was found and corrected and all filters were reweighed. The zero and calibration of the balance was checked after every fifth weighing. Any blank filter weight outside of the normal range of 90 to 110 mg resulted in immediate investigation.

A unique sample identification number was assigned to each filter. Fiber filters were placed in filter folders and Teflon filters were placed in petri dishes which contained the sample ID for shipment to and from the field.

3.3.2 Field Sampling

In the field, each filter was loaded into the sampler at the time the previous sample was removed. Sample start and stop times were controlled by mechanical or electronic timers and sample durations were quantified by elapsed time meters. All Teflon filters were handled while wearing disposable gloves. Fiber filters were handled on the edges with bare hands.

Average flow rates before and after filter exposure were measured for HIVOL and SSI samplers with a continuously recording Dickson Mini-corder. This device provided a constant trace over the sampling period so that the occurrence and duration of power or motor failures could be evaluated. The Mini-corder was calibrated at 5 flow rates every three months, when a motor or brushes were changed, or when successive calibration checks disagreed by 10% or more. The calibration standard was a variable resistance orifice calibrator which was in turn calibrated once per year with a Roots meter. Calibration was checked with the calibrated orifice by using a clean filter to provide flow resistance; this check was performed every other sample (approximately once each 12 days). Nominal flow rates were 1.4 and 1.1 m^3/min for HIVOL and SSI, respectively.

The Beckman SAMPLAIR dichotomous sampler was operated in a manual mode controlled by a master timer independent of the sampler's microprocessor unit. Initial flow rates through the FINE and COARSE filters were 15.0 and 1.67 l/min, respectively, and were measured with separate rotameters. Flow rates were also measured following sampling. Rotameters were calibrated at the factory and the total flow rate (sum of flows through FINE and COARSE samples) was subject to a one point check every other sample (approximately 12-day intervals) using a calibrated orifice meter. Sierra 244 and 244E dichotomous sampler flow rates were measured the same way.

The 1.67 l/min flow rate through the COARSE filter meant that approximately 10% of the FINE particulate matter was deposited on the COARSE filter. Corrections to the measured FINE and COARSE masses were made as part of the data processing step.

Sample volumes were calculated from the average of initial and final flow rates multiplied by the sample duration. Samples were collected for about 24 hours every sixth day. The nominal volumes of air pulled through HIVOL, SSI, and dichotomous samplers were 2000, 1600, and 22 m^3, respectively.

3.3.3 Sulfate and Nitrate Analysis

Automated colorimetry was used for the analysis of ions from HIVOL, SSI, FINE, and COARSE filters. All the analyses were done by EPA/EMSL. Their procedures are summarized briefly.

Filters were extracted (1/12th of an exposed filter for SSI and HIVOL, all of FINE and COARSE) in 40 ml of distilled deionized water by sonication for 30 minutes followed by centrifuging at 2000 rpm for 20 minutes. For HIVOL samples, one ml of each extract was poured into a specimen vial and the sample turntable rate was 40 samples per hour with 2:1 sample to wash-time ratio. The sample tray run at the beginning of each day was loaded with duplicate calibration standards. Quality control standards were placed in every tenth position.

Sulfate was determined using the methylthymol blue (MTB) method (Technicon, 1972). The extract was first passed through an ion exchange resin to remove the interferring cations. Then it was mixed with a solution of MTB and barium chloride at pH 3 to 4. Sulfate ions in the extract reacted with the barium to form barium sulfate, thereby lowering the ratio of barium to MTB. Sodium hydroxide was then added, raising the pH to 11 or 12. At high pH, barium and MTB form a blue-colored chelate. The excess uncomplexed MTB is gray. The amount of uncomplexced MTB, monitored colorimetrically at 460 nm, is proportional to the sulfate concentration.

Nitrate was determined using the cadmium reduction method in which the sample was mixed with ammonium chloride, then passed through a copperized cadmium column which reduced the nitrate to nitrite (Technicon, 1976). A mixture of N-(1-naphthyl)ethylenediamine dihydrochloride (NEDA), sulfanilamide and phosphoric acid was added to the sample. The nitrite and NEDA reacted to form a pink dye with a peak absorbance at 520 nm which was proportional to the nitrate concentration.

Interlaboratory and intermethod comparison results of this method (Mueller and Hidy et al, 1981) show it to be free of interferences and with excellent reproducibility.

3.3.4 Elemental Analysis

The elemental analysis of HIVOL and SSI filters was accomplished using inductively coupled argon plasma emissions spectroscopy (Lynch et al, 1980) according to USEPA (1978b). Elemental concentrations on HIVOL and SSI filters were reported in EPA data summaries for 11 different elements as shown in Figure 3.3.1 (USEPA, 1981a). To extract the elements, 1" x 8" of each filter was placed in a polypropylene centrifuge tube to which 12 ml of extracting acid (2.23 M HCl, 1.03 M HNO_3) was added. The mixture was ultrasonicated for 50 minutes and 28 ml of distilled deionized water was added to the tube. The mixture was centrifuged for 20 minutes at 2500 rpm. The clear solution was then transferred to a 30 ml acid-clean polypropylene bottle, taking care not to disturb the solids in the bottom of the tube. The analysis was done on a Jarrell-Ash Inductively Coupled Plasma Emission Spectrometer at EPA/EMSL. Two quality control standards were prepared from the stock calibration standards and run with each set of samples.

The FINE and COARSE membrane filters were analyzed by x-ray fluorescence analysis following the procedure described by Dzubay and Rickel (1978) at Lawrence Berkeley Laboratory. Several additional filter samples were analyzed by NEA Laboratories for this study for Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb.

X-ray fluorescence analysis is a non-destructive technique. Samples go through this analysis prior to the colorimetric analysis where they are destroyed. Atoms in the sample are excited from their ground states to higher energy levels by x-radiation from x-ray tubes. The energy emitted by atoms as they return to their normal ground level is characteristic of the emitting element and is used to quantitatively identify the element. Details on the replicate analysis and calibration procedures are not available in USEPA (1980). Elemental concentrations on FINE and COARSE filters are reported in EPA data summaries for 15 different elements as shown in Figure 3.3.1 (USEPA 1981a).

3.3.5 Carbon Analysis

Total and organic carbon were determined for a selected subset of SSI and HIVOL filters at Environmental Research and Technology, Inc. by the method of Mueller et al (1980). These measurements are not part of the routine IP Network analyses undertaken by EPA/EMSL.

A Dohrmann DC-50 carbon analyzer was used for the determination. A sample to be analyzed was loaded onto a platinum boat containing manganese dioxide. The boat was then advanced to a pyrolysis zone at 850°C where all carbonaceous materials were oxidized by the manganese dioxide. Organic carbon was determined by lowering the temperature to 550°C. The carbon dioxide thus generated was then hydrogenated catalytically to methane and measured using a flame ionization detector. Calibration of the instrument involved nulling with acidified distilled deionized water and span checking with 180 ppm and 360 ppm carbon standards consisting of potassium hydrogen phthalate solutions. Detector output was set to correspond directly to the carbon concentration of the standards. A separate punch from every tenth filter was reanalyzed to ensure precision of the analysis was maintained.

3.3.6 Optical Microscopic Analysis

Optical microscopic analysis of portions of the deposits on nineteen SSI filters and some source samples was performed by Boeing Aerospace Corporation's Fine Particle Laboratory. The details of the optical microscopic analysis applied to these selected SSI filter samples are described by Crutcher and Nishimura (1981) with their results of the analysis.

The particles from a 12 cm^2 section of each 8"x10" filter were removed by sonication in toluene and the extract was centrifuged. Portions of the particulate matter residue were mounted on slides for viewing under a polarizing microscope.

First, a qualitative identification of particle types common to the sample was made by moving the slide on the microscope stage and classifying the observed particle types by morphology, refractive index, color, birefringence, and association with other particle types.

The particle types identified were divided into five major categories with a number of subcategories:

- Minerals, including quartz, calcite, gypsum, clay and other minerals.
- Biological materials, including plant parts, pollen and spores, starch and other biological material.
- Industrial and transportation particles, including weathered industrial, calcium hydroxide, hematite (rust), hematite (industrial), glass, slag, paint spheres, tire wear, golden needle, lead oxide needle, hydrated cement, clinker, γC_2S, C_3S, and glass cement.
- Combustion products, including fused flyash, unfused flyash, charred wood, soot, oil soot, black carbonaceous spheres, black carbonaceous spheres, cenospheres, bagasse, black irregular, charred paper, magnetite spheres and coal.
- Particles not contained in other categories, including molybdenum disulfide and any other unidentified substances.

The particles were identified as members of specific categories based upon recognition of the features determined in the qualitative analysis; this recognition was made by the microscopist. The diameter of each particle was estimated by identifying which circle of a Porton graticule best approximated the projected area of the particle. Each successive circle of the graticule increases its diameter by 1.41 times that of the previous circle; nine circles were used for comparison ranging from 1 um to 16 um in diameter. The majority of the particles observed had optical diameters corresponding to the circles less than the 8 um diameter circle.

Each sample was moved across the center of the field of view and particles were identified and counted as they reached the eyepiece crosshairs until approximately 1,000 particles were included. The numbers of particles within each particle type and size range were totaled, multiplied by a density typical of the particle type (densities of minerals were obtained from Deer et al, 1966, while densities of other materials were derived from density gradient measurements of other researchers) and the volume of a sphere having the diameter of the Porton graticule circle corresponding to that size range. The masses achieved by this process were summed and the percent of this total comprised by each category was calculated by dividing the mass of particles so classified by this sum.

The following limitations of this method are realized:

- The process of removing particulate matter from the filter may result in some loss, dissolution, or preferential extraction of different particle types.
- One thousand particles is small compared to the total number of particles collected on the filter. If one assumes 1,000 particles of 8 um diameter and 2 gm/cm^3 density are counted, the total mass observed amounts to approximately .5 ug. This represents .0003% of the mass deposited on a typical HIVOL filter.
- Few particles are spherical and the adjacent size ranges differ by a factor of 2.8 in particle mass. Particles falling between ranges can have mass estimates differ from their true values by up to 50%.
- Only coarse particles (greater than 1 to 2 um optical diameter) are observed and counted. Therefore, the proportions of particles resulting from each category correspond only to the COARSE size fraction.

The uncertainties in particle source-type contribution estimates resulting from these limitations of optical microscopic analysis are difficult to quantify; no precision model incorporating all of them has yet been proposed. The portion of this uncertainty due to statistical counting error in the sample examined was calculated for each of these samples using the method of Crutcher and Nishimura (1978) for each particle type. This uncertainty could exceed a factor of 2 in a given particle category.

3.3.7 Accuracy and Precision of Analysis

Each of the procedures followed in the IP Network involves replicate analysis and audit components, the data from which can be used to estimate accuracy and precision over specified time periods. Though the collocated mass measurements presented later in this chapter give an idea of the mass concentration measurement precision which is attainable by following IP Network standard operating procedures, they do not tell what the relative precisions of individual measurements are. This must be done through the use of replicate analyses of measurements for specific sites and times.

Many comparisons of measurements are made in this report and conclusions are drawn when measures differ from each other. If the uncertainty intervals of two measurements do not overlap, then they significantly differ from each other and a cause of that difference can be sought. If the intervals do overlap, however, then no significant difference exists between them. Without knowing these intervals for the measurements being compared, it is impossible to determine the significance of differences or similarities among these measurements.

At this preliminary stage, very little Quality Control (QC) and Quality Assurance (QA) data from the IP Network have been compiled and summarized for those using the data for interpretive purposes. Such a summary is required if the interpretation of measurements by those who did not participate in their acquisition is to be meaningful. Baumgardner (1981) reports that such a summary will be issued in EPA's 1981 data summary.

3.4 Data Validation

The HIVOL, SSI, TOTAL, FINE and COARSE mass measurements used for the analyses in this report went through various validation steps which verified their acquisition according to prescribed procedures, their transfer through the data management system and their internal consistency with respect to each other. Some of these procedures were applied by EPA/EMSL to eliminate and flag suspect data. Additional criteria were applied to the resulting data set by the authors of this report. Both sets of procedures are outlined in this section. The EPA/EMSL mass concentration validation procedures are presented in USEPA (1980c). Validation takes place in the field, in the weighing laboratory, and at data processing.

Samples were invalidated by the field technician if:

- sampling did not start at 0000 ± 0030 local time,
- the sample duration was outside of the interval 24 ± 1 hr,
- post-sampling flow rates were 10% less than pre-sampling flow rates,
- flow rate calibration checks (scheduled for every other sample change) made before and after a sample was taken differed by more than ± 10%
- leaks around filter were indicated by a discolored edge, or
- the filter was damaged.

In addition to invalidating the sample under the above conditions, the field technician noted on the data card any emissions or meteorological conditions which might bias the measurement.

In the weighing laboratory, glass fiber filters were weighed in sets of 100. Five of these were reweighed by a different technician and if the reweights did not agree within prescribed tolerances, all weights for that set were invalidated until the filters were reweighed and the reweight test was passed.

For dichotomous samples, 5 to 7 filters were reweighed every day for each balance in operation. If the prescribed tolerances were exceeded, then all of the weights measured on that balance on that day were invalidated and the procedures were repeated for those filters.

At the data processing step, all records which were keypunched from the data forms were checked for faithful transcription. After association of mass and flow rate measurements and calculation of ambient mass concentration by a computer, the measurements were screened by:

- identifying negative or less than detection limit values,
- statistical outlier tests, and
- comparison of measurements from simultaneous samples in different size ranges.

Input data records associated with values flagged by this screening were examined and corrections to the data base were made when discrepancies were found.

Values which did not pass through this screen after the correction process was complete were:

- invalidated and removed if they were negative,
- flagged with as S if they were statistical outliers, and
- flagged with an R according to the criteria of Table 3.4.1.

Table 3.4.1

DATA VALIDATION FLAGGING CRITERIA

1\.

$$\text{If} \begin{bmatrix}\text{HIVOL}\\ \text{SSI}\\ \text{TOTAL}\\ \text{FINE}\\ \text{COARSE}\end{bmatrix} \text{value is} < \begin{bmatrix}20\\ 15\\ 15\\ 10\\ 5\end{bmatrix} \text{ug/m}^3\text{, or} > \begin{bmatrix}120\\ 100\\ 100\\ 40\\ 60\end{bmatrix} \text{ug/m}^3\text{, flag value.}$$

2. If SSI/HIVOL ratio is > 1.1 or < .4, flag both values.

3. If TOTAL/HIVOL ratio is > 1.1 or < .4, flag both values.

4. If TOTAL/SSI ratio is > 1.2 or < .8, flag both values.

5. If COARSE/FINE ratio is > 1.3 or < .3, flag both values.

The EPA/EMSL defined limits in Table 3.4.1 are empirical and are used only as a guide to more extensive validation; it is possible, though unlikely, that these limits are exceeded under ambient conditions.

For the purposes of this study, additional criteria were applied to remove some, but not all, flagged values from the data set used for the majority of the interpretive efforts. To remove all flagged values would have made the data too sparse to be of any use, but some of the discrepancies were so obvious that any interpretation of the data would have been severely compromised.

For the purposes of this report the measurements of HIVOL, SSI, TOTAL, FINE and COARSE for a site and day were removed by the authors if any of the following inequalities was found to be true:

$$\left(\frac{\text{COARSE}}{\text{HIVOL - FINE}}\right) < .3 \qquad 3\text{-}1$$

$$\text{If no HIVOL} \quad \left(\frac{\text{COARSE}}{\text{SSI - FINE}}\right) < .3 \qquad 3\text{-}2$$

$$\left(\frac{\text{HIVOL - SSI}}{\text{HIVOL}}\right) < -.15 \qquad 3\text{-}3$$

$$\left(\frac{\text{HIVOL - TOTAL}}{\text{HIVOL}}\right) < -.15 \qquad 3\text{-}4$$

Inequalities 3-1 and 3-2 state that the COARSE material, that within the 2.5 to 15 um range, must equal at least 30% of the material in the 2.5 to 30 um range for the set of samples to be accepted. The 30% value is arbitrary and was chosen because the IP data suggest it as a natural dividing point. Many samples, particularly those from the Phoenix and Birmingham areas, showed very low COARSE sample masses. The ratios of COARSE/(HIVOL - FINE) for these cities were in the neighborhood of .1 to .2, a very unlikely situation given the typical particle size distributions discussed in Section 2.2.

Inequalities 3-3 and 3-4 eliminate measurements for which the mass of particulate matter in the 0 to 15 um range exceeds the mass in the 0 to 30 um range by more than 15%, a reasonable tolerance for measurement error.

The resulting subset of the inclusive sampling dates listed in Appendix A.1 contains 2,087 HIVOL, 771 SSI, and 1,509 dichotomous (TOTAL, FINE and COARSE) values out of a possible 2,675 HIVOL, 1,045 SSI and 1,960 dichotomous samples (Suggs et al, 1981b).

The analyses presented in Chapters 7 and 8 this report used the data set filtered by inequalities 3-1 to 3-4. Statistical data summaries were received from EPA for the treatments in Chapters 5, 6 and 9; these were based on the EPA validated data which were not subject to the screening of inequalities 3-1 to 3-4. The appropriate notation will be made when screened and unscreened data are used.

The extensive data validation procedures outlined here have resulted in individual measurements which are internally consistent. The criteria have taken their toll, however, in leaving large gaps where samples have been invalidated. The validation and flagging process is necessary, but the lack of measurements resulting from it in many situations introduces a sampling error due to the reduced number of values, particularly for simultaneous measurements. As the network monitoring progresses and the standard operating procedures become ingrained, fewer samples will be invalidated and the size of the validated data base will grow.

3.5 Precision and Accuracy of Size-Classified Mass Measurements

The purpose of this section is to identify, and quantify where possible, the biases to mass concentrations in the IP Network and to estimate the precision attainable with these measurements from collocated sampling.

Though the HIVOL sampler has been the mainstay of suspended particulate matter sampling for nearly three decades, recent studies show that it is subject to certain biases other than those already noted which, if not considered, will appear to be properties of the ambient aerosol rather than consequences of the sampling method. An examination of these studies is useful in estimating the bias introduced into the IP Network's HIVOL measurements and in indicating studies which need to be carried out with regard to the other IP samplers. These studies include the effects of:

- Carbon and copper emissions and recirculation into the sampled airstream of the HIVOL or other concurrently running samplers.
- Deposition and removal of particulate matter during passive sample exposure periods.

The motor of a HIVOL sampler contains a copper commutator which turns between carbon brushes. The abrasion of these surfaces causes copper and carbon particulate matter to be entrained in the air exiting the HIVOL. It is possible that some of this particulate matter finds its way onto the sampling substrates, thus biasing the ambient air measurements. In the IP Network, carbon was measured as part of this study on selected glass fiber filter samples. Copper is routinely quantified both on selected glass fiber and Teflon filter samples. Contributions from both of these substances can add to the mass concentration measured on a filter. Bias due to HIVOL emissions is a possibility and the maximum likely contribution must be quantified.

Fortunately, studies of these emissions have been performed by other researchers. Countess (1974) measured 150 ug/m^3 carbon in the output of a typical HIVOL sampler. He injected known concentrations of dioctylphthalate (DOP) into the HIVOL discharge and measured the amount collected on the filter under various ambient airflow conditions. He found the greatest recirculation occurred with the HIVOL blower removed from its housing in a horizontal position; .1% of the HIVOL DOP emissions were collected. The maximum carbon concentration bias is therefore .15 ug/m^3, a quantity below the lower quantifiable limits of carbon measurements.

The worst case recirculation efficiency of .1% is valid for copper emissions as well, and, since the commutator wears at a slower rate than the brushes, the contribution to the sample mass is negligible. King and Toma (1975) demonstrated that under normal operating conditions, a HIVOL can collect as much as ten times the ambient copper levels as a result of blower emissions. This recirculation was reduced substantially when a tight seal between the HIVOL blower and the housing was formed so that no recirculation could travel through the housing. Because the dichotomous sampler inlets are normally at least 1 m above and 2 m to the side of the HIVOL exhaust, the copper contribution is probably negligible to FINE and COARSE samples under most conditions. Significant contributions to the HIVOL and SSI samples is a possibility, however. High copper values in the .1 to .6 ug/m^3 range should be suspected of being contaminated (King and Toma, 1975), except in situations where a known industrial source of copper, such as a copper smelter, might be the cause of elevated copper concentrations. The IP Network chemical analysis data show many copper (Cu) concentrations on HIVOL and SSI samples in this range, while FINE and COARSE Cu measurements taken simultaneously are substantially lower. Cu contamination from the HIVOL motors is a viable possibility.

In the IP Network HIVOL sampling configuration, a HIVOL filter could remain in an idle sampler for up to six days prior to and after sampling. During this idle period, wind blows particle laden air through the HIVOL housing with some of those particles depositing on the filter. This is termed passive mode deposition. McFarland et al (1979b) have quantified this deposition as a function of particle size, wind speed and ambient concentration. They found that the deposition rate increases with increasing values for any one of these variables. For example, in an 8 km/hr wind, McFarland et al (1979b) found 8 ug of the 5 um particles they generated deposited on the HIVOL filter for each 1 ug/m^3 concentration of these particles in the sampled air over a 24-hour period. This increased to 40 ug/24-hr for 1 ug/m^3 of 15 um particles and to 100 ug/24-hr deposited for 1 ug/m^3 concentration of 30 um particles. The fraction of total suspended particulate matter sampled by the HIVOL greater than 15 um is in the vicinity of .33 (Pace, 1979b). If the ambient air contains 100 ug/m^3 total suspended particulate matter, then the deposition bias on the filter during the 6-day standby period would be about 6 ug/m^3 for 15 um particles and 13 ug/m^3 for 30 um particles according to McFarland's data. The actual bias in the mass concentrations could be calculated by integrating McFarland's deposition function times the ambient particle size distribution by the method of Section 2.2. Ambient experiments have been performed, however, which provide more useful estimates of passive deposition.

Bruckman and Rubino (1976) found positive biases ranging from 5 to 28%, with an average of 15% when comparing collocated HIVOL samples from 6-day and 0-day standby periods. Blanchard and Romano (1978) found a range of 2 to 48% with an average of 13% (by inverting the sampler they seem to have eliminated the deposition bias). Chahal and Romano (1976) measured a range of -5 to 29% with an average of 7%. Swinford (1980) found a -5 to 25% range with an average of 10%. These experimental results agree with the wind tunnel measurements of McFarland et al (1979).

Sweitzer (1980) examined several passively loaded HIVOL filters from Peoria and Decatur, Illinois with an optical microscope and found 90% of the particles to have optical diameters greater than 10 um with some diameters as large as 60 um. This qualitative particle evaluation identified fly ash, sulfate particles and coal fragments on the Peoria samples and corn starch balls, bundles and grains on the Decatur samples. These were similar to presumed emissions from nearby industrial sources.

Thanukos et al (1977) have raised the concern that some of the particulate matter collected by the HIVOL is removed by wind blowing through the sampler during the standby period following sampling. They compared TSP measured by a standard HIVOL with that obtained from a HIVOL preceded by an Andersen Cascade impactor; presumably the impactor did not allow wind to remove particles. For TSP concentrations less than 150 ug/m^3 they found the geometric mean of unprotected HIVOL measurements to be 5% less than the geometric mean of measurements by the wind-protected HIVOL with a 1-day standby period following sampling. Swinford's (1980) tests confirm this. This bias is not significant for IP Network samples.

Deposition during passive periods can cause samples taken with the HIVOL to be significantly biased. Normally, approximately 10% of the average TSP can be attributed to this bias, but this can be significantly higher for individual measurements made in atmospheres with a great quantity of large particles.

Passive deposition experiments have not yet been performed on HIVOL(SSI) and dichotomous samplers. Presumably, the size-selective inlets will prevent the larger particles responsible for this deposition from being blown into the sampler, but the bias is impossible to estimate without wind tunnel and ambient tests similar to those performed for the HIVOL. Such tests need to be planned in the near future.

The best estimation of the precision attainable from the samplers used in the IP Network is from the results of collocated sampling of the same ambient concentrations by similar instruments.

McKee et al (1972) conducted a HIVOL sampling collaborative testing program with twelve laboratory groups participating. The samplers were equally spaced on a flat, 465 m^2 rooftop at a height of 15 m above ground level. Each group weighed its own filters, calibrated its own samplers, and measured its own flow rates. The sampling time was measured by the referee of the study. The mean coefficient of variation for the results from 11 of the 12 groups (the results from one group were deemed outliers) was 3.8% for particulate matter concentrations in the 70 to 140 ug/m^3 range. The mean coefficients of variation of mass measurements made with two collocated standard HIVOL samplers in another study (Camp et al, 1978) was 4.1% in the 50 to 180 ug/m^3 range.

Several collocated sampling studies have compared the dichotomous sampler models used in the IP Sampling Network. Shaw et al (1981) compared Beckman samplers and concluded:

> "...over a broad mass range, fine fraction aerosol mass can be collected using the standard commercial inlets with a reproducibility of 5% or better. Coarse fraction aerosol mass can be collected with a reproducibility of 10% or better except for very light mass loadings (less than 200 ug). Fine and coarse masses can be collected with a reproducibility of 5% or better."

They found that the mass measurement precision dominates the precision attainable below approximately 200 ug (or 8 ug/m^3) loadings. This uncertainty rises rapidly below this point for the beta gauge mass measurements Shaw et al (1978) made and passes ±50% at 4 ug/m^3 concentrations.

Grantz (1981) compared collocated measurements from the Sierra 244 and Beckman samplers by linear regression and found slopes (intercepts) of .73 (12.9), .79 (6.13) and .53 (7.11) for TOTAL, FINE and COARSE, respectively, when the Beckman measurement was the independent variable. The correlation coefficients were low, .71, .77 and .53, respectively. Grantz (1981) does not present the data used to calculate these parameters, but the agreement between most individual values was probably not within ±10% with such high intercepts, slopes different from one, and low correlation coefficients.

Pashel et al (1980) ran collocated Sierra dichotomous samplers in the vicinity of two steel mills and found percent differences (calculated as the ratio of the differences to the average of the two measurements) ranging from -40% to +40% for TOTAL, -59% to +65% for FINE and -72% to +67% for COARSE at one site. At another site the ranges were -49% to +90% for TOTAL, -10% to +115% for FINE and -200% to +15% for COARSE. Pashel et al (1980) noted several sampling difficulties, such as dirty inlet tubes and a buildup of particulate matter around the collection nozzle.

Collocated sampling studies with the HIVOL(SSI) have not been reported.

Three collocated sampling sites have been established in the IP Network to assess network precision, one at 500 S. Broad St. in Philadelphia (PAPHA), one at ARMCO Coke Plant Gate in Middletown, Ohio (OHMII) and one at ARMCO Research (OHMIB) in Middletown. Data are available for HIVOL, TOTAL, FINE and COARSE measurements at Philadelphia, PA and for HIVOL and SSI measurements at Middletown, OH. Figures 3.5.1a-d present scatterplots and linear regression parameters for each of these comparisons. Though the correlation of HIVOL measurements is quite good at both PAPHA and OHMII, a bias of 9% seems to exist between samplers at both sites as evidenced by the linear regression slopes. The average of ratios of paired samples for HIVOL is .97 and 1.02 for PAPHA and OHMII, respectively, so the difference in slopes is probably an artifact of the regression process. The precision is still acceptable for most HIVOL measurements, however. The average of absolute percent differences is 6.5% at PAPHA and 4.7% at OHMII. Eighty percent of all paired measurements at PAPHA are within ±10% of each other and all are within ±20%. The nominal reproducibility of HIVOL sampling using IP Network

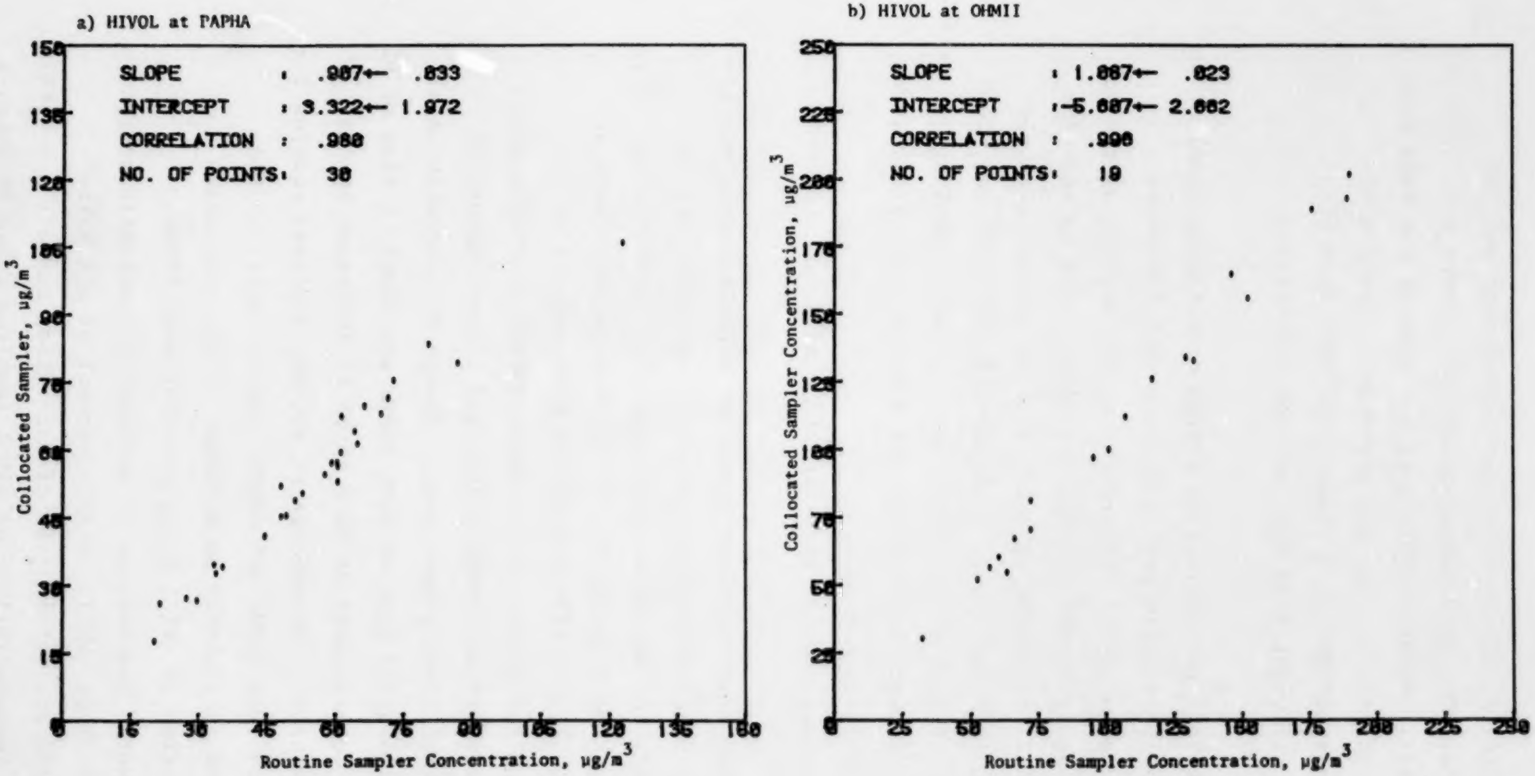
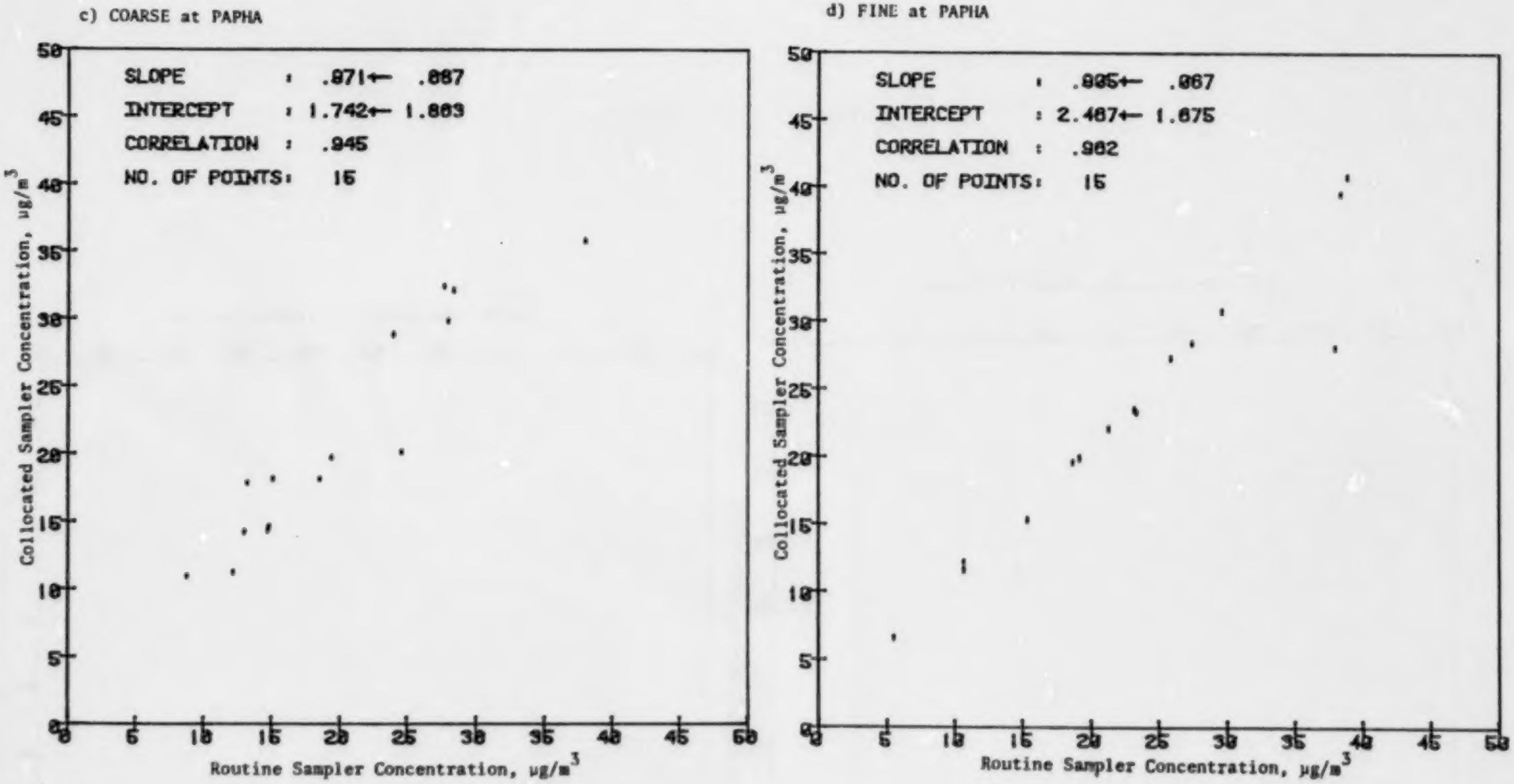


Figure 3.5.1 a-f Scatterplots of Collocated Measurements for HIVOL in Philadelphia (a), HIVOL in Middletown (b), COARSE in Philadelphia (c), FINE in Philadelphia (d), TOTAL in Philadelphia (e) and SSI in Middletown (f)



c) COARSE at PAPHA

d) FINE at PAPHA

Figure 3.5.1 (Continued)

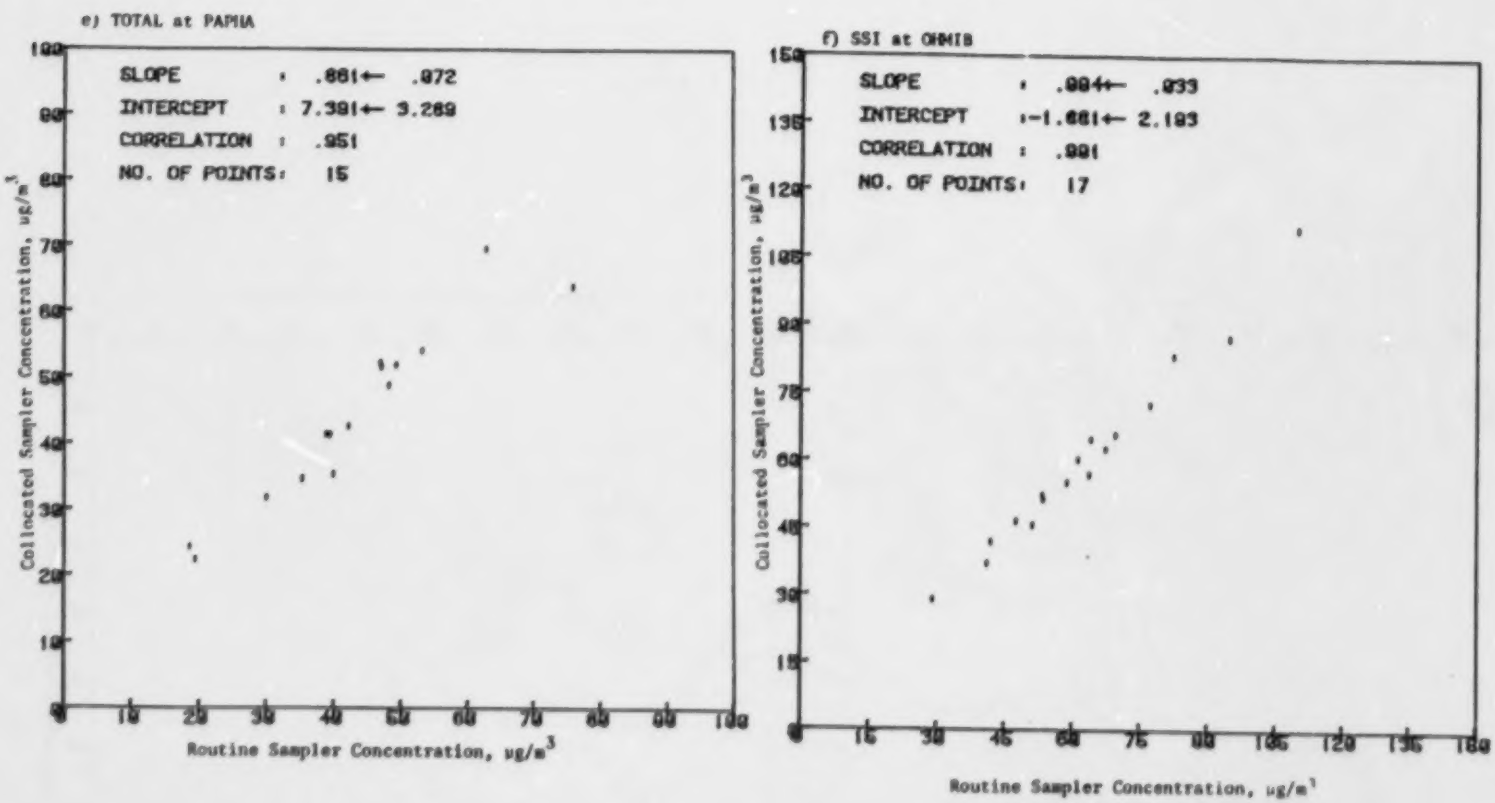


Figure 3.5.1 (Continued)

standard operating procedures is in the neighborhood of ±5%, which is comparable to the precisions previously cited.

The slope of the collocated PAPHA COARSE measurements' regression line does not show the bias exhibited by the HIVOL comparison, though the correlation is not nearly as good. The average of absolute percent differences is 11.5%. Fifty-three percent of the paired measurements are within ±10% of each other, 87% are within ±20% and all are within ±30%. The COARSE measurement uncertainty using IP Network standard operating procedures is in the neighborhood of ±10%, agreeing with Shaw et al (1981) measurements.

The FINE reproducibility is illustrated in Figure 3.5.1d. The average absolute percent difference between values is 7%; 80% of the values are within ±10% of their average, 93% are within ±20% and all are within ±30%. The average ratio is 1.04.

The TOTAL scatterplot shows an average ratio of 1.05, an average absolute percent difference of 9%, and 60% of the values within ±10%, 93% within ±20% and all within ±30% of their average.

The SSI average ratio is .96, absolute percent difference is 4.5% and all values are within 11% of their average.

More collocated sampling needs to be done in different parts of the network to assure that the precision estimates made here have wider application. These estimates show that precisions within ±10% are attainable, and in the SSI and HIVOL cases within ±5%, for IP Network measurements. This is a snapshot of the entire network, however, and individual measurements may have greater or lesser uncertainties associated with them.

This chapter is an archive of information about the measurement process which should be used as an aid in interpreting data from the IP Network data base. It brings to light several features of the existing data base and suggests some additions to the measurement and reporting process that could be made to enhance the usefulness of IP Network data.

- Most sampling site locations seem to be representative of the study scales for which they were selected. Site surveys should be standardized, completed, compiled and made available for all IP Network sites. The site-type classification scheme is still subjective and it is likely that some sites are misclassified. The types of samplers (e.g. Beckman or Sierra) and their installation and removal dates should also accompany this survey.

- The change in SSI and HIVOL filter media after the beginning of 1980 could result in differences between sulfate, nitrate and mass measurements which are products of the measurement process rather than an environmental cause. The exact dates on which the change took place at each site should be tabulated, and some consideration should be given to a well planned, executed and documented switch back to the Microquartz filter which seems to minimize sampling artifacts.

- The routine IP Network measurements comprise mass, elements and ions on HIVOL, SSI and TOTAL filters which are acquired via a comprehensive set of procedures and analytical methods. What is lacking is documentation concerning the quality control and auditing of these procedures. Blank, standard and replicate checks should be used to estimate the measurement precision of individual data items and these should be recorded in the data base and included in data reports. Network audit results should be summarized to provide a statistical measure of the measurement accuracy for each observable.

- The data validation procedure to which IP Network mass data are submitted identifies many internal inconsistencies as well as extreme cases; the total number of these cases amounts to a large portion of the data base. For the purposes of this report, several of these flagged values were deleted. The number and types of flags should be summarized with the data capture statistics for each site. Data validation procedures have been applied only to mass measurements; (no validation flags appear on reports of chemical composition) and should be extended to ion and element measurements.

- Tests on HIVOL samplers show that copper emissions from the motor can interfere with Cu measurements from nearby samplers and that deposition on the filter during standby periods can interfere with mass measurements. The emissions should be eliminated by filtering or ducting sampler exhaust. Passive deposition should be minimized by shortening exposure times during the sampler standby mode. Passive deposition measurements on HIVOL(SSI) and dichotomous samplers should be carried out.

- The comparison of collocated HIVOL measurements in the IP Network is similar to comparisons in other networks showing average differences between simultaneous samples of less than 5% of the average mass concentration. Similar results are obtained for HIVOL(SSI) samplers. Collocated dichotomous samplers have been shown to attain average differences of less than 10% of the average IP mass concentration. Collocated measurements between Beckman and Sierra samplers need to be made; since these two samplers are assumed to be equivalent for IP Network measurements, a test is required to support that assumption.

CHAPTER 4

URBAN AREAS IN THE IP NETWORK

At the time of this report, the Inhalable Particulate Matter Sampling Network measured concentrations in 26 heavily populated areas of the United States.

This chapter presents general meteorological and statistical information for those areas that are related to the particulate matter concentrations. In seven cities, Birmingham, AL; Phoenix, AZ; Denver, CO; Buffalo, NY; Philadelphia, PA; Houston, TX; and El Paso, TX; the industrial source types and their geographical locations with respect to receptors have been identified on maps. This descriptive information will prove useful when the relationship between chemical composition of the aerosol and its sources is examined in Chapter 9 of this report.

4.1 General Meteorological and Statistical Information

Table B.1 of Appendix B lists typical (the average of approximately 30 years of data) annual average meteorological measurements in the urban areas of the IP Network. The first three columns show variations in average, maximum and minimum temperatures. The averages range from 44.1°F (Minneapolis) to 70.3°F (Phoenix). The maxima vary from 53.8°F (Minneapolis) to 85.1°F (Phoenix), and the minima fall between 34.3°F (Minneapolis) and 58.0°F (Houston).

Precipitation is lowest (less than 10 inches) in Phoenix and El Paso, and highest (greater than 40 inches) in Birmingham, Hartford, Atlanta, Boston, Baltimore, Raleigh, Houston, and Richmond. The sunniest areas (more than 70% of the time) are Phoenix, Los Angeles, Denver, El Paso, and Salt Lake City, while Seattle, Portland, and Pittsburgh enjoy the available sunshine only 50% of the time. Thirty year average wind speed for most urban areas is in the range of 14 to 18 km/hr with a low speed of 10 km/hr in Phoenix and a high of 20 km/hr in Boston. Most daytime relative humidities are between 50 to 60%.

Seasonal degree days follow the temperature averages with low values (less than 2000 DD) in Birmingham, Phoenix, Los Angeles, Honolulu, and Houston and high values (greater than 6000 DD) in Denver, Hartford, Des Moines, Chicago, Detroit, Minneapolis, Buffalo, and Cleveland. Snowfall is non-existent in the Arizona and California urban areas, minimal in Texas, Oregon and North Carolina, and heavy in Denver, Hartford, Boston, Minneappolis, Cleveland, Pittsburgh, and Salt Lake City. Snowfall levels in Buffalo are extremely high.

Because of the long averaging times involved, the data in this table obscure relationships between meteorological factors and individual particulate matter concentrations. The data in this table are intended for use as a screening device to decide whether or not a more detailed examination of specific meteorological or emissions measurements available at the time the samples were taken is warranted.

For example, degree days are related to wintertime heating requirements and the concomitant combustion of wood, oil, coal or natural gas. Differences in wintertime fine particle carbon concentrations, should they be measured, between areas with vastly different degree day values could be due to this source type. Similarly, elevated wintertime concentrations of sodium and chloride in Buffalo, where average snowfall is 93 inches, might be caused by the salting of roads whereas this would be an unlikely contributor to elevated concentrations of these elements in Houston.

Table B.2 of Appendix B presents general population, area and industrial activities information about each of the urban areas. Once again, this information is for screening purposes rather than to provide a direct relationship between anthropogenic activities and suspended particulate matter concentrations. Populations of the metropolitan areas and the space which they encompass vary substantially. Population density is probably a better indicator of potential emissions which might affect the measured concentrations. Highest population densities (greater than 10,000 people/mi^2) are in the eastern and midwestern cities of Washington, D.C., Chicago, Boston, Baltimore, Detroit, St. Louis, Buffalo, and Phiadelphia. One western city, San Francisco, falls into this category. Lowest population densities (less than 3,000 people/mi^2) are in Phoenix, Kansas City, Raleigh, El Paso, and Houston. The general summary of major industries gives some idea of what the possible industrial suspended particulate matter emissions might be.

Many other summaries of descriptive information would be helpful as pointers to more detailed information when the manmade progenitors of measured pollutant concentrations are sought. Average mixing heights, geography, climatological cycles, number of vehicle miles traveled, gasoline and fuel oil consumption for the periods over which samples were taken would be helpful. Much of this information is available and should be summarized as part of the IP Network's data record.

One of the most important issues deriving from a new standard for inhalable particulate matter will be the extent to which industrial sources are responsible for any violations of that standard which are observed at particular monitoring sites. Some initial estimates of industrial contributions in typical urban areas can be obtained from the chemical concentrations acquired through the IP Network. For these data to be meaningful, however, it is necessary to gain a more detailed understanding of the industrial source character of individual urban areas.

4.2 Industrial Emissions in Several Urban Areas

Though it is possible to hypothesize the potential contributors to measured suspended particulate matter chemical concentrations, there is no substitute for a knowledge of the types of sources within an urban area and the locations of those sources with respect to the receptors. All urban areas will contain emissions from area sources such as motor vehicle exhaust, residential combustion of gas, oil, or wood, and resuspended geological material from roadways and vacant lots.

The specific area sources most likely to affect the measurements at a specific sampling site are those in immediate proximity to it. These roadways, homes and open areas are best identified from the individual site surveys described in Chapter 3.

Industrial point sources, however, are not homogeneously distributed throughout an urban area. Emissions are often from stacks which provide more opportunity for pollutants to be transported further than those from ground-level sources. The contributions from point sources are highly dependent on source-receptor geometry with the receptor being downwind of the source during the sampling period (Gordon, 1980). When conclusions are drawn concerning the likely sources of chemical concentrations measured by the IP Network, as they will be in Chapter 9 of this report, it is important to know the types of point sources contributing to an urban area and their locations with respect to the samplers.

In several cases, this has been done in great detail. Portland, OR and St. Louis, MO have detailed maps showing their major industrial point sources. IP Network sites ORPOA and ORPOB identified in Table A.1 of Appendix A, correspond to sites 1 (exactly) and 3 (nearby) in Watson (1979) and IP sites MOSLA and MOSLB correspond to sites 119 (nearby) and 111 (exactly) in Dzubay (1980). On a neighborhood scale, Grantz (1981) presents a map for the IP monitoring sites in the vicinity of ARMCO Steel in Middleton, OH. IP Network sites OHMIA, OHMIB, OHMIC, OHMID, and OHMII correspond to Grantz' sites 8, 6, 5, 4 and 3 respectively. Many other such maps may exist in more obscure references which remain to be identified.

Seven such maps showing major industrial sources, their types of emissions, and relationship to IP sampling sites have been prepared for this study and are presented here. The cities were chosen because they are representative of the western, eastern, southwestern, and southern parts of the United States and contain varying degrees of industrial activity. The basis for identifying and locating the sources was the condensed point source listing of the National Emissions Data System (USEPA, 1980a).

The information in this listing is supplied to the EPA by state and local air pollution agencies. The listing contains the industry name and address, its location in UTM coordinates, estimated annual emission rates for all criteria pollutants, including TSP, and a source classification code (SCC)(USEPA, 1972) which identifies the process or function which causes the emissions. Several of these processes may be present in a given industry.

In certain cases, the SCC is not adequate to identify the process. A Standard Industrial Classification (SIC) (U.S. Office of Management and Budget, 1972), which identifies the primary product or activity of an industry, is used in these cases. Only one SIC is assigned to a company even though that company may have several types of processes, and therefore several SCC. The SCC is preferable as an identifier of particulate matter source types.

As part of this study, NEDS inventories for Philadelphia, Birmingham, Phoenix, Buffalo, and Los Angeles metropolitan areas were obtained from EPA/OAQPS. NEDS inventories from Denver, Houston, and El Paso were obtained from the Colorado and Texas state agencies as part of other projects (Heisler et al, 1980a; Heisler et al, 1980b; Heisler et al, 1981) and were adapted to the format of this study. Presumably the information in the state-generated inventories and federal inventories are the same, though feedback from officials in Colorado, Texas and Pennsylvania indicate that the state inventories are more accurate because they are more frequently updated.

Because so many point sources (literally thousands, most of them being small boilers in apartment houses, schools and hospitals which should be treated as area sources) are listed in the inventories, a selection criteria was devised to narrow those chosen to the most likely contributors. For Birmingham, Phoenix, Buffalo, and Philadelphia, only sources with TSP emission rate estimates exceeding 5 tons/yr were drawn from the inventories for location on maps. In Houston, El Paso, and Denver, many of the point sources which met this criterion were more similar to area sources than to point sources. For these areas, a 50 tons/yr cutoff was used. The Los Angeles inventory is nearly as large as those of all other cities combined and it was only half completed by the time resources available in this project were expended on it, so results are not presented here.

Records in the NEDS inventories are dated 1975 to 1977 and it is recognized that TSP emission rates calculated at that time would be substantially different today. For example, a source in Philadelphia, the NE Incinerator, is no longer in operation even though NEDS shows it emitting 356 tons/year. However, the NEDS emission rates are of value in that they reflect the potential contributions of different source types even though the recorded emission rates may not be current in all cases.

Staff members of the Texas Air Control Board and Philadelphia Air Management Services reviewed the emission inventories in El Paso, Houston, and Philadelphia and found the point source types and locations specified by the NEDS to be correct, for the most part, though some errors in location and present level of activity were found. This local agency review is still needed for the Birmingham, Phoenix, Denver and Buffalo inventories.

Since measurements at IP sampling sites include elemental and ionic concentrations, and in a few special studies might involve elemental and organic carbon measurements as well as particle size segregation, knowledge of the major chemical species and the dominant size range (FINE or COARSE) constituting the emissions from these potential urban sources is required to relate them to the ambient concentrations. After the source types in the seven urban areas were identified, the aerosol source characterization literature was reviewed to determine the major chemical component and dominant particle size of each source.

Table 4.2.1 presents the potential sources of inhalable and fine suspended particulate matter, the dominant particle size and chemical composition of emissions from those sources according to the given references, and a number corresponding to the point source (•) on one of the maps in Figures 4.2.1 to 4.2.7.

Each number represents a facility which could (but not necessarily does) contribute to the given particle size and chemical concentrations measured at receptors. The IP sampling sites(ⓧ)are also located on the maps with numbers which correspond to the site codes in Table 4.2.2. Reference to the site survey summary, Table 3.1.3, gives an idea of the likely areas sources affecting each site.

With the information in Table 4.2.1 and the geographical relationships of sources to receptors specified in Figures 4.2.1 to 4.2.7, it is possible to state some hypotheses concerning the

TABLE 4.2.1

POTENTIAL SOURCES OF INHALABLE AND FINE SUSPENDED PARTICULATE MATTER IN U.S. URBAN AREAS

Source Type	Birmingham AL	Phoenix AZ	Denver CO	Buffalo NY	Phili PA	Houston TX	El Paso TX	Dominant Particle Size	Major Chemical Species	Reference
1. Geological										
a. Rock Crusher, grinding	24, 28	A, 04, 05, 06, 07, 08		08		03, 22	01, 02	COARSE	Al, Si, Fe, Ti	Watson (1979)
b. Asphalt Roofing material		04, 05, 06	11		15	26		COARSE	Al, Si, Fe, Ti	Watson (1979)
c. Street Dust	A*	A	A	A	A	A	A	COARSE	Al, Si, Fe **EC, OC, Ti	Rahn et al (1976) Taylor (1964)
d. Concrete batching					09		01, 07, 09	COARSE	EC, OC Ca, $SO_4^=$ Na, Cl	
e. Abrasives	12				11			COARSE	EC, OC, Ca	
2. Transportation										
a. Auto leaded gas	A	A	A	A	A	A	A	FINE	Pb, Br, Cl EC, OC	Pierson et al (1976) Shah (1981)
b. Auto nonleaded gas	A	A	A	A	A	A	A	FINE	EC, OC	
c. Diesel truck	A	A	A	A	A	A	A	FINE	EC, OC	
d. Diesel train	A	A	A	A	A	A	A	FINE	EC, OC	
e. Misc. (ships, air, tires, brakes	A	A	A	A	A	A	A	FINE		
3. Fossil Fuel										
a. Residual Oil Combustion	02, 04, 06, 07, 08, 09, 13, 14, 15, 16, 17, 19, 22, 23	01, 02	10	01, 02, 05, 08, 11, 12, 13, 14, 15, 16, 20, 21, 22, 23, 24, 26, 27, 28, 34, 35, 36, 38	05, 07, 08, 11, 13, 14, 15, 17, 22, 24, 26, 27, 30, 37, 44, 45, 52, 58	01	01, 04, 06	FINE	EC, OC, V, Ni $SO_4^=$	Von Lehmden et al (1974) Watson (1979)

TABLE 4.2.1 (Continued)

Source Type	Birmingham AL	Phoenix AZ	Denver CO	Buffalo NY	Phili PA	Houston TX	El Paso TX	Dominant Particle Size	Major Chemical Species	Reference
b. Distillate Oil Combustion	A, 25	A, 01	A, 03, 06	A	A, 11	A	A	FINE	EC, OC, $SO_4^=$	
c. Anthracite Coal Combustion				42	06, 21, 29, 47, 49, 50, 51, 54, 56	25		FINE	Al, Si, FE, Na, OC, EC, As	Coles et al (1979)
d. Natural Gas Combustion	25	01	03		40	01 to 25, 32	03, 04	FINE	EC, OC	
e. Bituminous Coal Combustion	08		04	17, 29, 31, 32, 33, 37, 39				FINE	EC, OC	
f. Fuel Oil Combustion						02, 04, 05, 06, 11, 13, 36	03	FINE	EC, OC	
g. Refinery Gas Combustion					11	03		FINE	EC, OC	
4. Forest Products Industry										
a. Wood Products[a]					03	24, 27, 28		COARSE	EC, OC	
b. Lime Kiln & Production	07					01, 02, 03, 10	02, 03,	?	?	
c. Paperboard Containers Manufacturing				20	02, 48, 53, 55			COARSE	EC, OC	
d. Bark Boiler						02		FINE	EC, OC	
e. Bark Dryer						02		FINE	EC, OC	
f. Recovery Boiler						04, 10		FINE		

TABLE 4.2.1 (Continued)

Source Type	Birmingham AL	Phoenix AZ	Denver CO	Buffalo NY	Phili PA	Houston TX	El Paso TX	Dominant Particle Size	Major Chemical Species	Reference
5. Vegetation										
a. Feed & Grain Handling	20, 26	09, 10, 11, 12, 13, 14, 15		07, 25, 30, 43	04, 16, 25, 33	04, 24, 29, 30, 37		COARSE	EC, OC, Si	Capar et al (1978)
b. Sugar Cane Processing					14			?	EC, OC	
c. Pollen	A	A	A	A	A	A	A	COARSE	OC	
d. Malt				09						
e. Fertilizer Production						02, 03, 04				
6. Heavy Industry										
a. Refinery Oil Heater					11		05, 06	FINE	EC, OC, V	
b. Coke Oven	01, 07, 08 25, 27, 29, 32			05, 13, 14	40	03		FINE	EC, OC	Barrett et al (1977)
c. Mineral Handling^b	03, 04, 21 28, 31	04, 05, 06, 07, 08,	01, 02, 07, 08, 09, 11	03, 10	02, 03, 10, 11, 36, 41, 43, 59			COARSE	EC, OC, Mn, Al, Si, Fe	
d. Copper Smelting	14				01, 12, 34		01	FINE	Cu, Al, S, Pb, Zn	Schwitzgebel et al (1978)
e. Lead Smelting & Production	14		05		38		01	FINE	Pb, S, Na, Cl, Fe	Mamuro et al (1979)
f. Aluminum Smelting	14	03			42			FINE	Al, F	
g. Zinc Galvanizing	11, 14				31, 32		01	FINE	Zn	
h. Iron & Steel Foundries	01, 02, 06, 07, 08, 09, 13, 14, 15, 16, 17, 19, 23, 25, 27 29, 30, 32			01, 05, 06, 13, 14, 40	40	03, 15, 25, 36	03	FINE	Fe, Zn, Cu Cr, Mn	
i. Aluminum Melting Furnace					42			FINE	S, Al, K, Na, Cl, Fe	Mamuro et al (1979)

TABLE 4.2.1 (Continued)

Source Type	Birmingham AL	Phoenix AZ	Denver CO	Buffalo NY	Phili PA	Houston TX	El Paso TX	Dominant Particle Size	Major Chemical Species	Reference
j. Blast Furnace[c]	01, 05, 07, 08, 18, 25, 27, 28, 29, 30, 32	04, 05		05, 13, 14	40			FINE	Fe, Mn, Zn	
k. Carbon Black Furnace					18			?	EC, OC	
l. Gas Heater					11			FINE		
m. Coating Oven					20			?	?	
7. Miscellaneous										
a. Carpet Making					39			COARSE	?	
b. Chemical Preparation[d]	09	04		11, 12	11, 18, 19, 28	01, 02, 03, 04, 06, 07, 08, 09, 10, 11, 32		FINE	?	
c. Paint Production				11	58			FINE	?	
d. Material Manufacturing[e]	10			18, 19	15					
e. Incinerator[f]				41	23, 35, 57	01, 04, 11, 13, 31, 32, 33, 34, 35, 38		FINE	EC, OC, Zn, Pb, Al, Cl, Cd, Cu	Greenberg et al (1978)
f. Cement, Clay Manufacturing	04, 22, 24, 28, 30	04, 05				22	01	?	?	

TABLE 4.2.1 (Continued)

Source Type	Birmingham AL	Phoenix AZ	Denver CO	Buffalo NY	Phili PA	Houston TX	El Paso TX	Dominant Particle Size	Major Chemical Species	Reference
g. Non-Clay Refactory				04				?	?	
h. Fluid Crackers						01, 02, 03, 04, 05	05, 06	?	?	

---

[a] Includes sawmill production.

[b] Includes metal fabrication, petroleum processing, gypsum, asphalt rotary dryer, asphalt concrete, manganese ore handling, ferromonganese alloy processing.

[c] Includes iron, steel, tin blast furnace.

[d] Includes plastic manufacturing, molybdenum-sulfate roasting, PVC production, agricultural pesticide manufacturing, detergent.

[e] Includes pumping equipment, motor vehicle parts and accessories, scrap and waste material.

[f] Includes municipal incinerator and industrial incinerator, trench burner.

**EC is Elemental Carbon, OC is Organic Carbon.

*A signifies an area source.

Numbers under each city heading refer to the locations of the industrial emissions points in Figures 4.2.1 to 4.2.7.

References are listed in Appendix C.

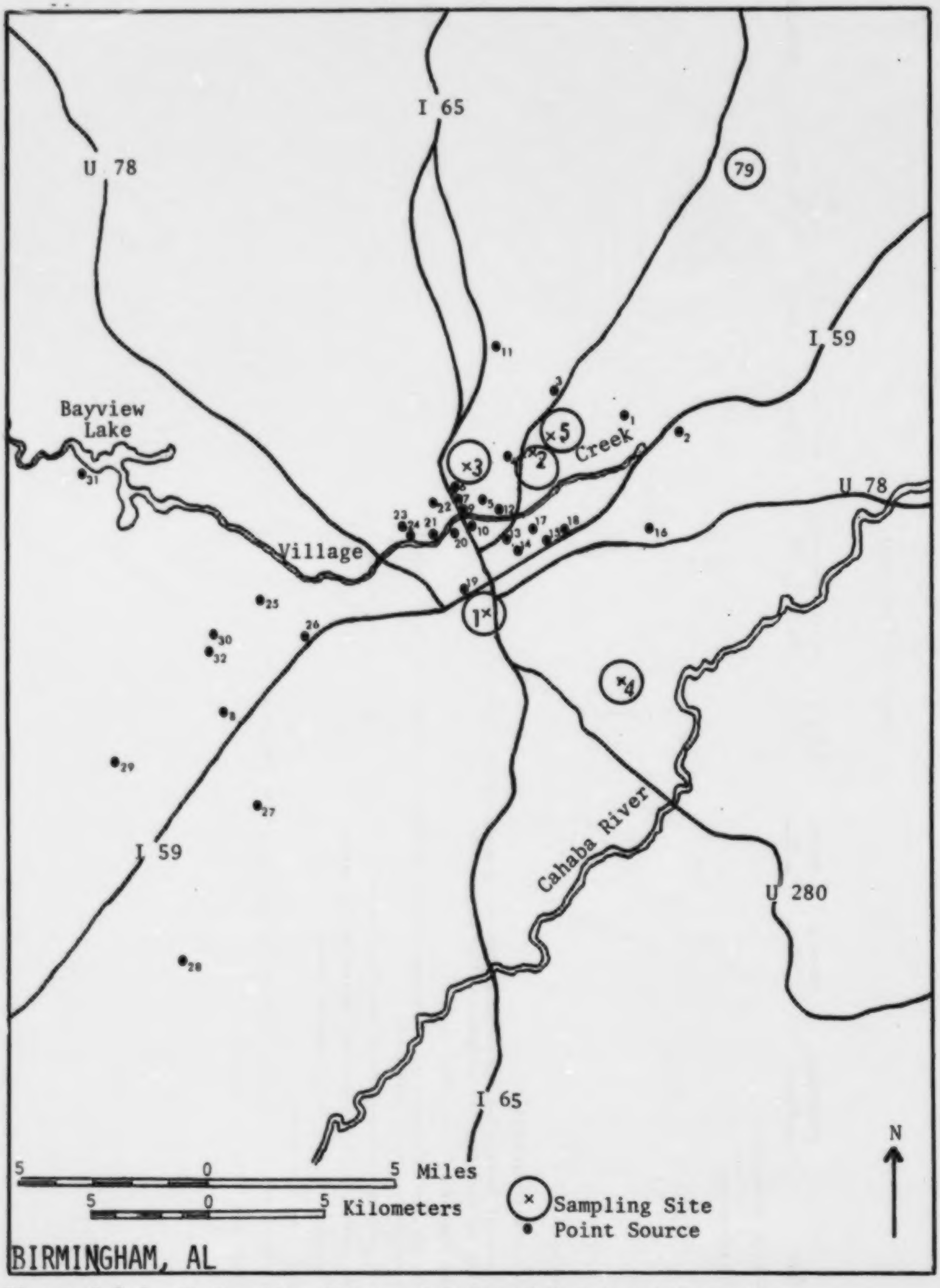

I 65
U 78
79
I 59
Bayview Lake
Creek
U 78
Village
Cahaba River
I 59
U 280
I 65
×3
×2
×5
1×
×4
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
5 0 5 Miles
5 0 5 Kilometers
× Sampling Site
● Point Source
N
BIRMINGHAM, AL

Figure 4.2.1 IP Sampling Sites and Industrial Point Sources in Birmingham, Alabama

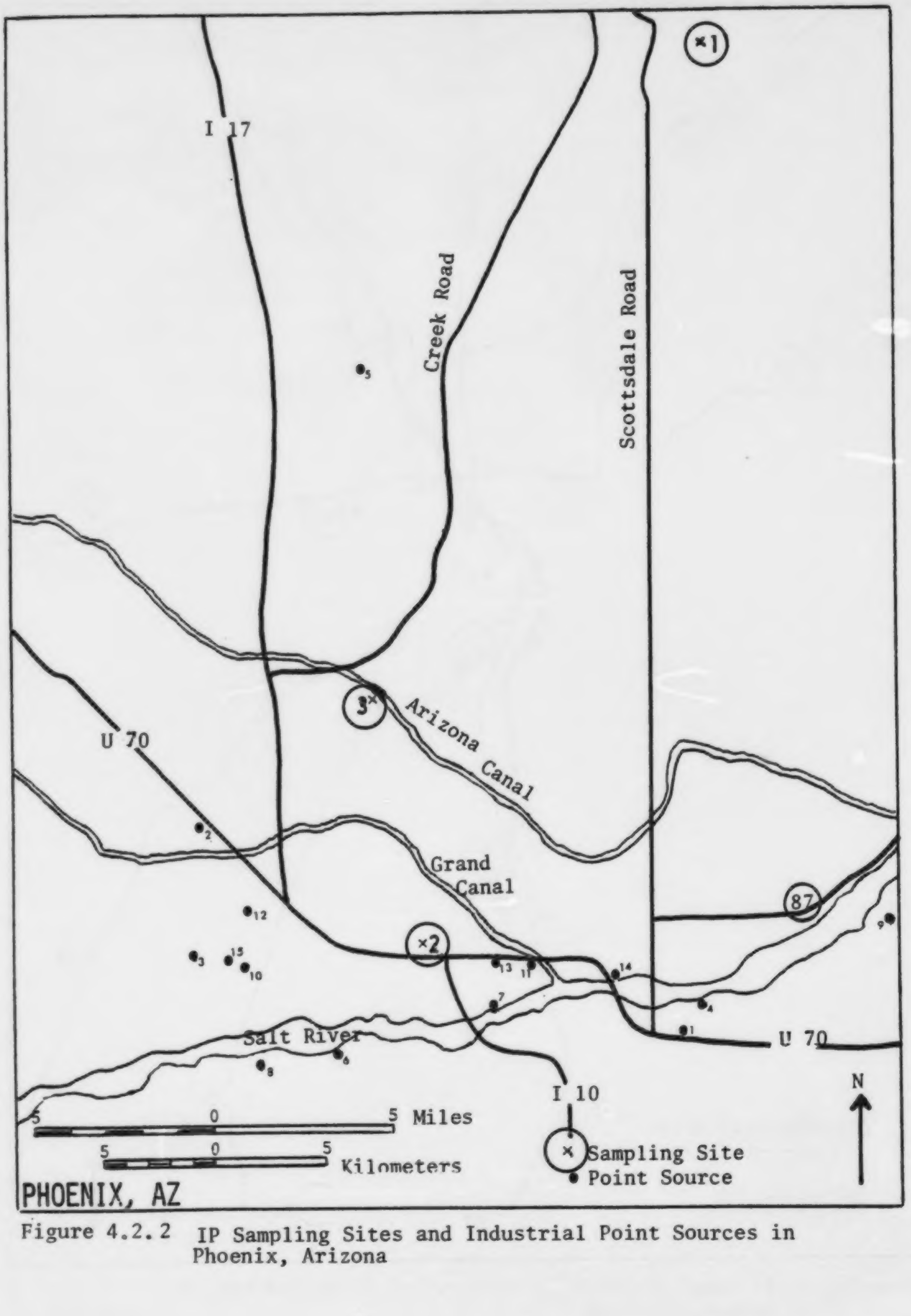

×1
I 17
Creek Road
Scottsdale Road
5
3×
Arizona Canal
U 70
2
Grand
Canal
87
12
×2
9
3
15
10
13
11
14
7
4
1
U 70
Salt River
6
8
I 10
N
5
0
5
Miles
5
0
5
Kilometers
Sampling Site
Point Source
PHOENIX, AZ

Figure 4.2.2 IP Sampling Sites and Industrial Point Sources in Phoenix, Arizona

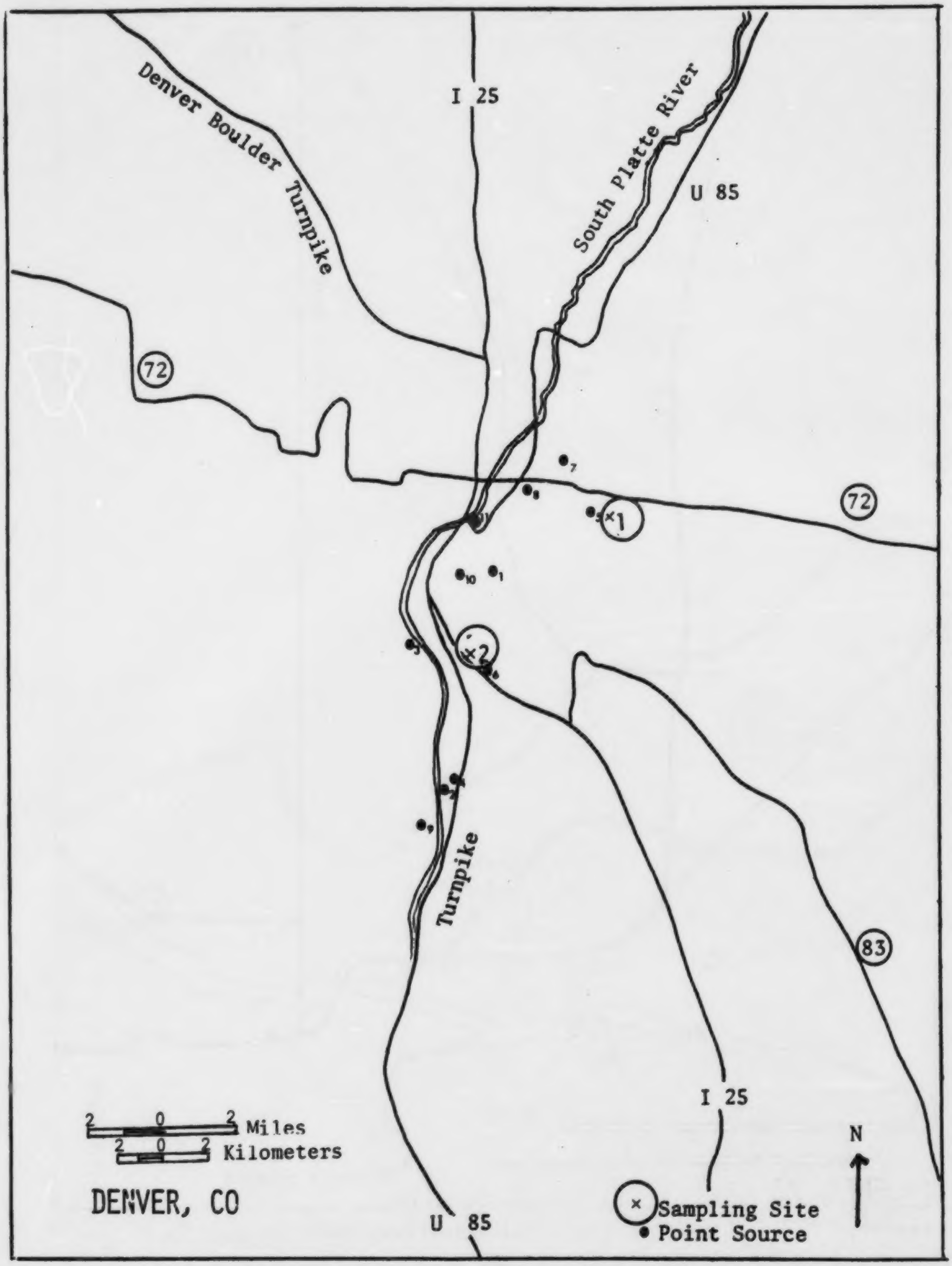
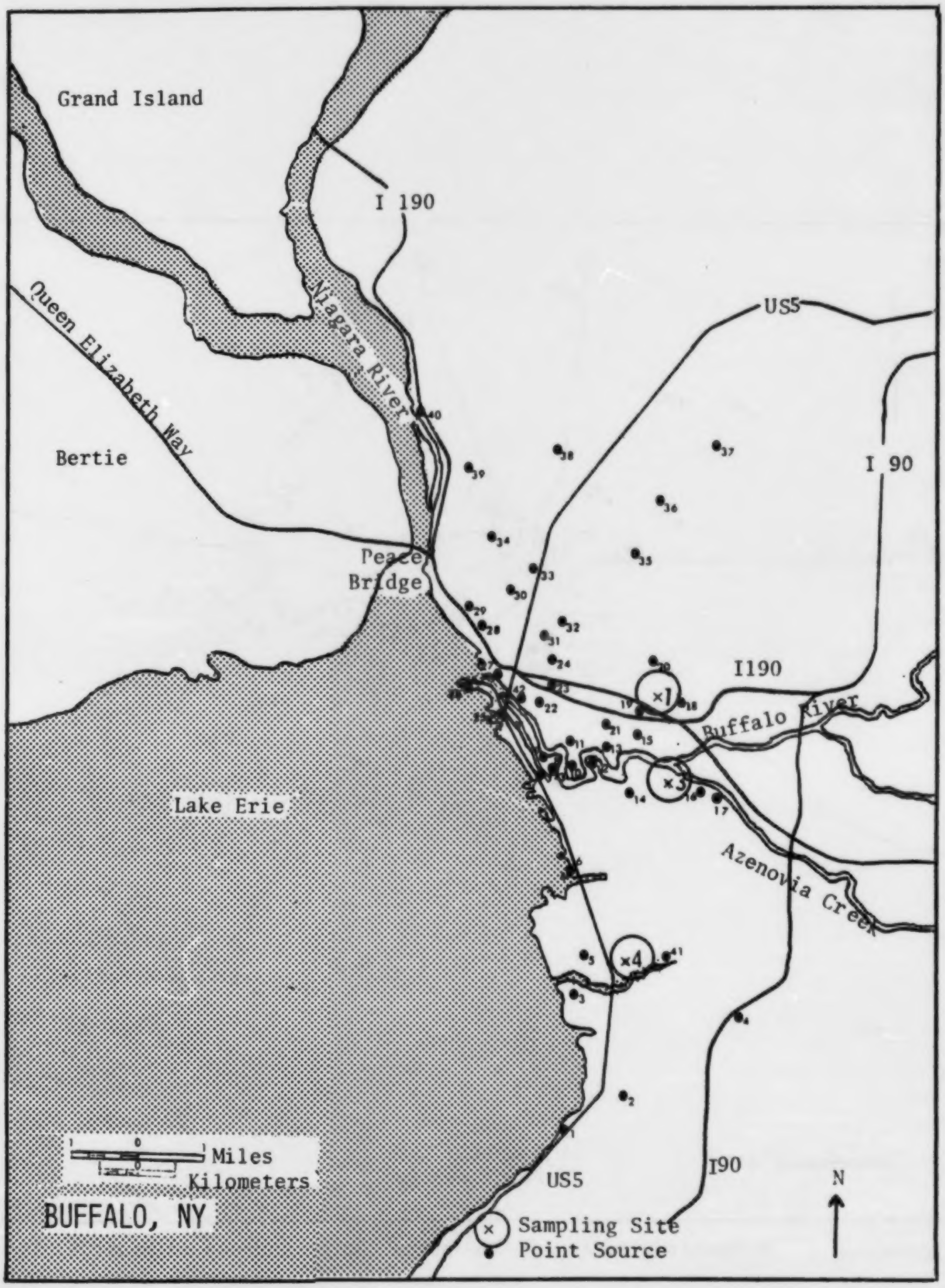

Denver Boulder Turnpike
I 25
South Platte River
U 85
72
72
1
2
3
4
5
6
7
8
9
10
Turnpike
83
I 25
2 0 2 Miles
2 0 2 Kilometers
DENVER, CO
U 85
× Sampling Site
● Point Source
N

Figure 4.2.3 IP Sampling Sites and Industrial Point Sources in Denver, Colorado



Grand Island
I 190
Niagara River
Queen Elizabeth Way
Bertie
US5
I 90
I190
Peace Bridge
Lake Erie
Buffalo River
Azenovia Creek
×1
×3
×4
1
2
3
4
5
11
13
14
15
16
17
18
19
20
21
22
23
24
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
I90
US5
1 0 1 Miles
0 Kilometers
BUFFALO, NY
× Sampling Site
● Point Source
N

Figure 4.2.4 IP Sampling Sites and Industrial Point Sources in Buffalo, New York

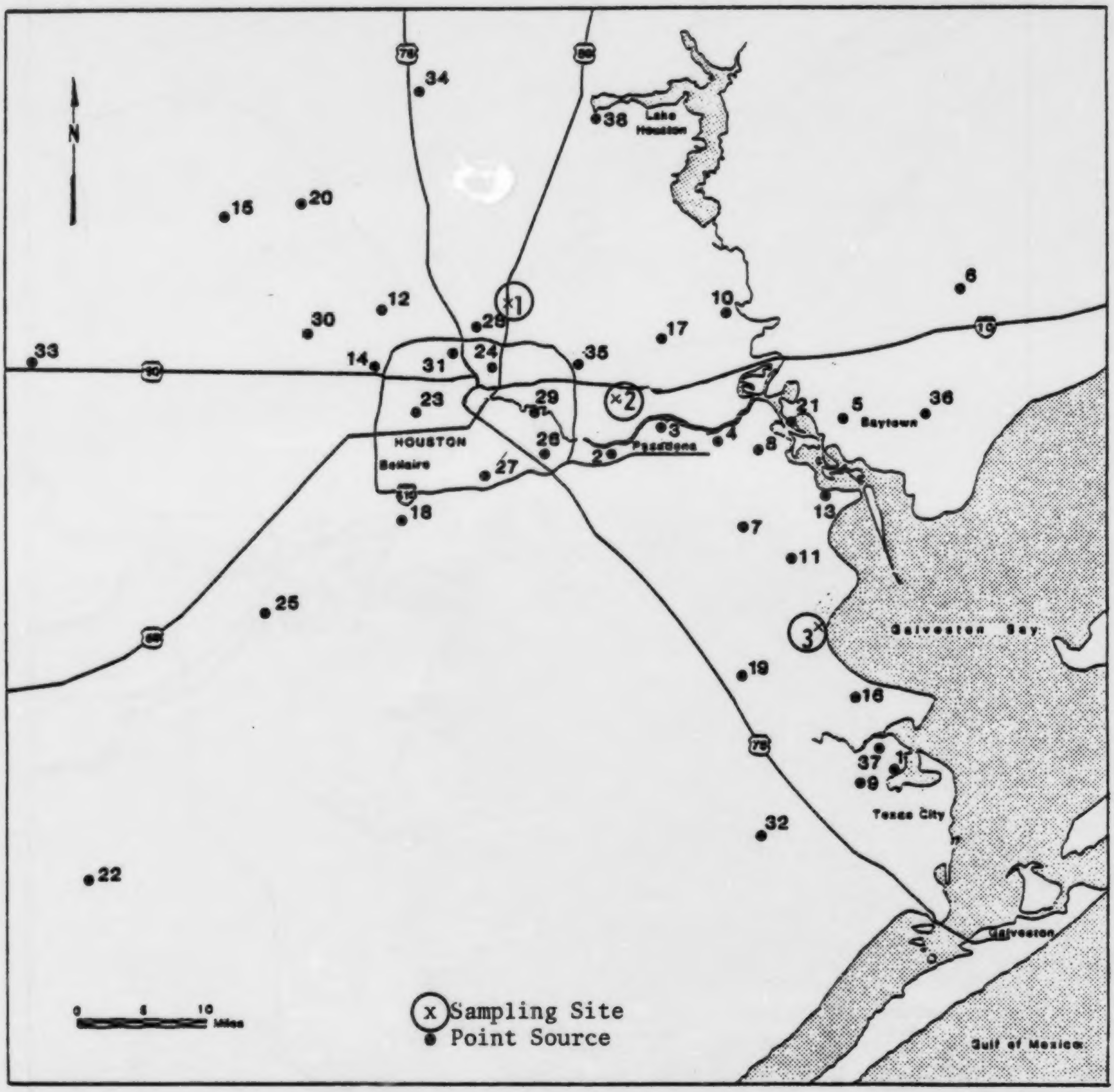

N
34
38
Lake Houston
15
20
6
12
1
28
10
17
30
33
14
31
24
35
10
23
29
2
21
5
36
Baytown
HOUSTON
3
26
2
Pasadena
4
8
Bellaire
27
610
18
13
7
11
25
3
Galveston Bay
19
16
37
9
Texas City
32
22
Galveston
0
5
10
Miles
x Sampling Site
● Point Source
Gulf of Mexico

Figure 4.2.5 IP Sampling Sites and Industrial Point Sources in Houston, Texas

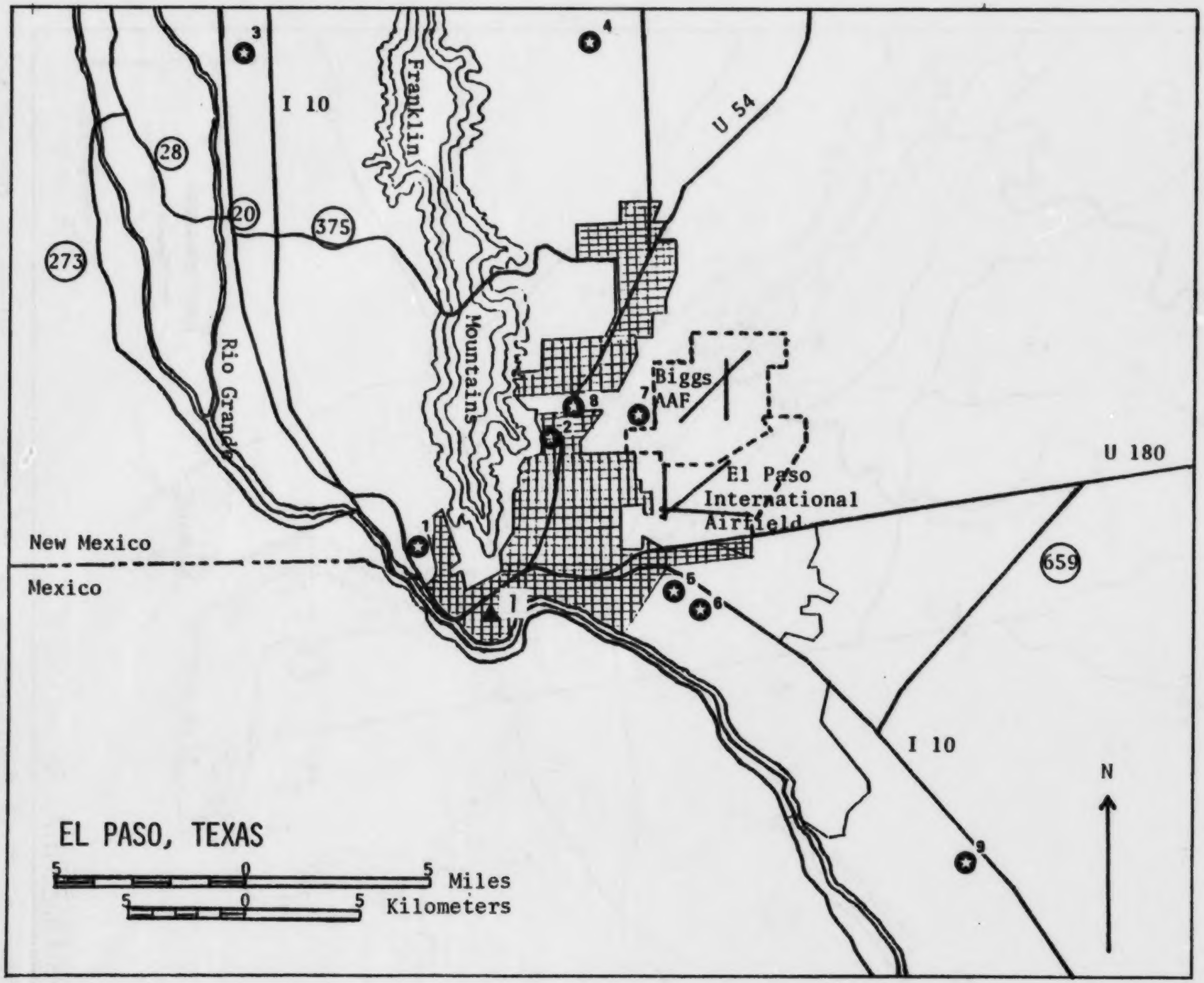

EL PASO, TEXAS
5 0 5 Miles
5 0 5 Kilometers
N
I 10
U 54
U 180
I 10
28
20
375
273
659
Franklin
Mountains
Rio Grande
Biggs AAF
El Paso International Airfield
New Mexico
Mexico
1
2
3
4
5
6
7
8
9
I

Figure 4.2.6 IP Sampling Sites (▲) and Industrial Point Sources (✪) in El Paso, Texas

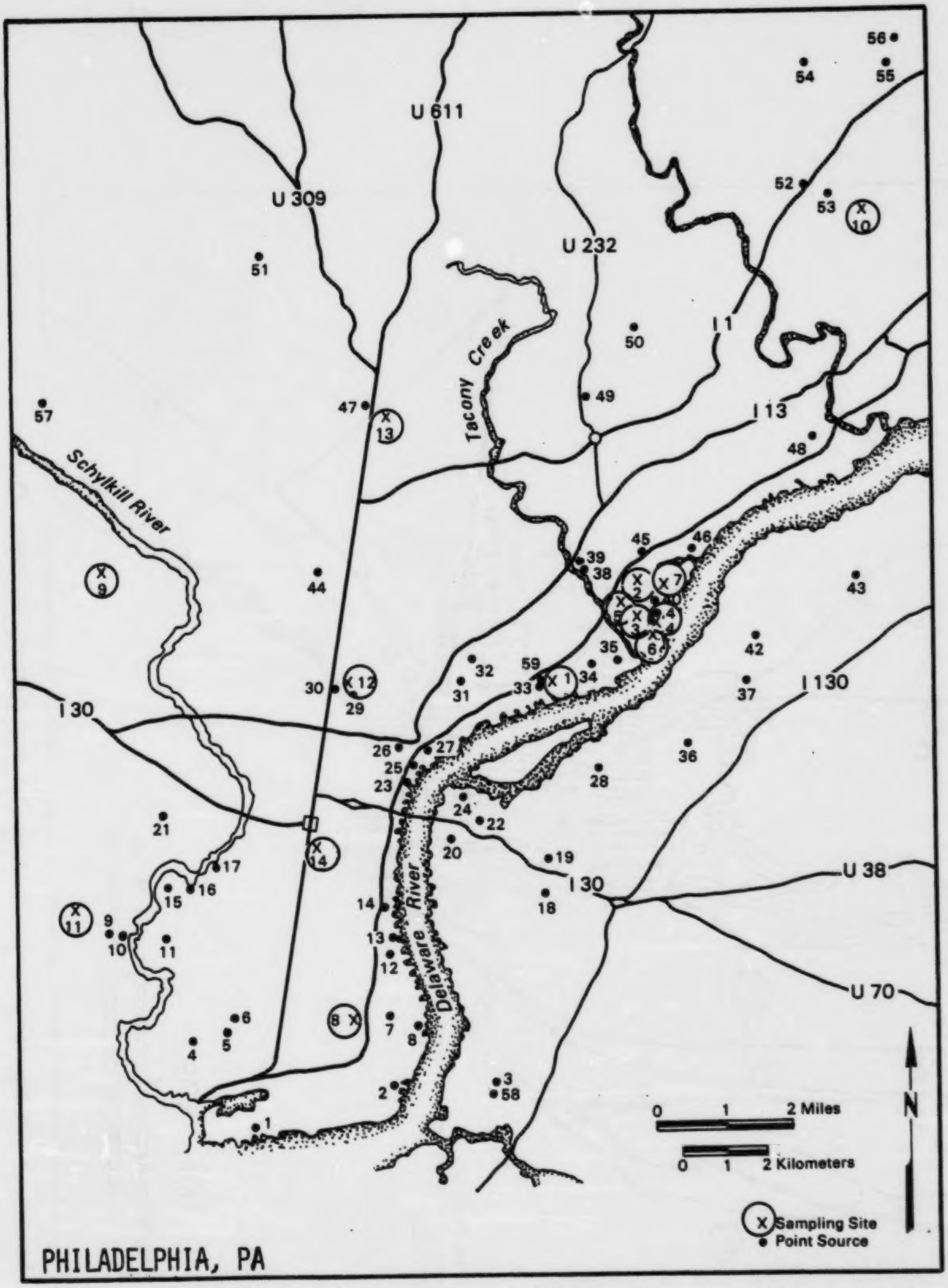

PHILADELPHIA, PA
U 611
U 309
U 232
I 1
I 13
I 30
I 130
U 38
U 70
Tacony Creek
Schylkill River
Delaware River
0 1 2 Miles
0 1 2 Kilometers
N
Sampling Site
Point Source

Figure 4.2.7 IP Sampling Sites and Industrial Point Sources in Philadelphia, Pennsylvania.

TABLE 4.2.2

IP SAMPLING SITES IN SEVEN URBAN AREAS

City, State	Map ID	Site Code	Site Name
Birmingham, AL	1	ALBIA	South Birmingham
"	2	ALBIB	Inglenook
"	3	ALBIC	North Birmingham
"	4	ALBID	Mountain Brook
"	5	ALBIE	Tarrant City
Phoenix, AZ	1	AZPHA	Carefree
"	2	AZPHB	Maricopa County Health Dept.
"	3	AZPHC	North Phoenix
Denver, CO	1	CODEA	Downtown
"	2	CODEB	Gates Rubber Company
Buffalo, NY	1	NYBUA	P. School No. 26
"	2	NYBUB	Big Sister Sewage Treatment Plant
"	3	NYBUC	P. School No. 28
"	4	NYBUD	Wilmuth Pump Station
Houston, TX	1	TXHOA	Aldine Mall Road, CAMS 8
"	2	TXHOB	CAMS 1
"	3	TXHOC	Seabrook
El Paso, TX	1	TXELA	Tillman
Clint, TX	2	TXELB	High School
Philadelphia, PA	1	PAPHB	Allegheny
"	2	PAPHI	St. John's Catholic Church
"	3	PAPHJ	Pilot Freight Motor Company
"	4	PAPHK	N.E. Wastewater Treatment Plant
"	5	PAPHL	T&A Pet Shop
"	6	PAPHM	N.E. Transfer Station
"	7	PAPHN	Bridesburg Recreation Center
"	8	PAPHD	S.E. Water Treatment Plant
"	9	PAPHC	Belmont Filter Plant
"	10	PAPHE	North East Airport
"	11	PAPHG	Presbyterian Home
"	12	PAPHH	Temple University
"	13	PAPHF	H. Gratz College
"	14	PAPHA	500 S. Broad

difference in chemical concentrations that should be observed between sampling sites and urban areas if certain industrial point sources are making significant contributions to fine and inhalable suspended particulate matter loadings. If these differences are found in the receptor measurements, then there is a good possibility that the sources may be contributors and further work should be specified if it is deemed desirable to confirm and to quantify those contributions. If significant differences are not found between sampling locations with different source characteristics, then the point sources with unique chemical characters are probably not major contributors compared to the more homogeneously distributed and common area sources.

One difficulty with this approach is that many of the emissions listed in Table 4.2.1 are the products of combustion and have no distinct chemical character other than their elemental and organic carbon content. This does not allow them to be distinguished at the receptors, and since routine carbon measurements are not made (and cannot be made on the sampling substrates presently used in the IP Network), an upper limit estimate of their contributions is not yet possible. In spite of this limitation, Table 4.2.1, Table 4.2.2 and Figures 4.2.1 to 4.2.7 contain a substantial amount of information about the possible and impossible source-receptor relationships.

Table 4.2.1 shows that the seven cities under consideration contain a large number of point source types as well as the usual area source types. Reading across the rows horizontally gives an idea of the number of source types in all of the urban areas. Rock crushing is prevalent in the western cities of Phoenix and El Paso, but not so common in the eastern cities. Major (recall that smaller units are not listed) residual oil combustion sources are concentrated in the eastern and southern cities. Feed and grain handling are minimal in Denver and El Paso while fertilizer production occurs only in Houston. Mineral handling and iron and steel foundries are sources common to several cities. Coal combustion is most prevalent in Philadelphia and Buffalo while most of the forest products operations are in Houston. Coke ovens are found in Philadelphia, Houston, and Buffalo. Philadelphia has the largest concentration of smelting operations.

Table 4.2.1 provides an idea of the particle sizes to be expected from different primary sources. The COARSE particle samples should receive their major contributions from geological material, wood and paper products, feed and grain processing, pollen, and mineral handling. Though other sources contribute some COARSE particulate matter, their contributions to the FINE samples should be greater than their contributions to the COARSE samples. Most of FINE contributors are point sources, though the residential heating and motor vehicle area sources also play their role.

Concerning chemical composition, the COARSE particulate matter concentrations should be rich in the geologically-related species of Al, Si, Fe, and Ti, with additional concentrations of carbon from feed and grain handling and pollen. In certain cases, mineral handling operations near a receptor site may raise the concentration of a particular element in which the particular mineral or ore being handled is enriched.

The FINE chemical concentrations will not present such a rich variety of chemical concentrations. The primary constituents of most fine particle sources are organic and elemental carbon. In certain cases, smelters or steel operations will contribute Al, Pb, Cu, Zn, Fe, and Mn to this fraction. Pb and Br can be expected from automobile exhaust and V and Ni will often be contributed by residual oil combustion. Naturally, some geological elements will be collected in the FINE particles. FINE particulate matter concentrations will also receive significant contributions which do not result from the primary emissions summarized in Table 4.2.1. Sulfate, nitrate, and a certain amount of the organic carbon found (Stevens et al, 1978) in ambient samples has been shown to result from the conversion of vapors to particles in the atmosphere. Thus, even though a large variety of sources emitting sulfate and nitrate do not appear in Table 4.2.1, concentrations of these species should be expected on ambient samples.

Reading down the city columns of Table 4.2.2 and relating the source locations to the receptor locations for individual urban areas by using the appropriate maps of Figures 4.2.1 to 4.2.7, intimates the types of chemical species which would be observed if the nearby sources were making contributions to each receptor.

In Birmingham, AL, all sites except site 4 are surrounded by a number of industrial point sources and might be expected to receive some contributions from them. Because there are a large number of iron and steel foundries and blast furnaces, chemical concentrations for Fe, Mn, Cr, and Zn are expected to be higher at sites 1, 2, 3, and 5 than at site 4. Residual oil burning is associated with the industrial activities which would elevate V, Ni and carbon concentrations. The zinc smelter (11) would contribute Zn to sites 3, 2, and 5 more than to sites 1 and 4, particularly with wind directions from the north or northwest. The transportation activities associated with the industry would contribute to organic carbon, elemental carbon, Pb and Br concentrations. Site 4 is a suburban residential site which is the best reference with which to compare concentrations at the other sites.

Compared to Birmingham, the population (referring to Table B.2 in Appendix B) in the Phoenix metropolitan area is twice as high but there is much less industrial activity. The major industries in Phoenix are feed and grain handling, mineral handling, rock crushing and aluminum smelting. Thus, point sources could be expected to make their major contributions to the COARSE particles. Site 2 should receive the greatest contributions from most sources including the rock crushers, mineral handling, feed and grain facilities and automotive emissions from major highways. Site 2 should see higher concentrations of Al, Si, Fe, Ti, Mn, and organic carbon in the COARSE and Pb and Br in the FINE than should be seen at the other sites. The aluminum smelter (3) may contribute Al to the FINE under westerly wind conditions. Residual oil combustion is low, Ni and V concentrations should not be as high as in other cities with more of this activity. Site 1 is a rural remote site which can be used as a background reference for the other two sites.

Denver is another city with few major industrial point sources. Mineral handling and the lead smelter (5) constitute the major operations. The population of Denver is high and the population density as shown in Table B.2 in Appendix B is twice as high as in Phoenix. Also, the location of the city of Denver is unique; it is elevated and surrounded by mountains. The amount of COARSE particulate matter and chemical species like organic carbon, elemental carbon, Mn, Al, Si, V, Ni, and Fe might be elevated at sites 1 and 2 due to the mineral handling facilities. The proximity of Pb smelters to site 1 could affect the Pb measured. Because of the high population density downtown, the area sources, like transportation and street dust contributions, might be elevated. Denver has exhibited a significant photochemical contribution and possible contributions from uninventoried wood combustion (Courtney et al, 1980, Heisler et al, 1980a, 1980b). FINE concentrations of elemental and organic carbon could be due to these sources. Neither site 1 nor 2 is an adequate reference site so it will be difficult to determine increments due to urban-scale sources in Denver.

The population of Buffalo is lower than that of Phoenix and Denver but the population density is very high; the weather is also very cold. This might cause FINE organic carbon, elemental carbon concentrations due to residential heating and Pb and Br concentrations due to motor vehicle exhaust to be elevated. Buffalo contains the largest number of coal combustion facilities, and FINE As concentrations might be elevated if they were contributors. Residual oil combustion units are widespread, and FINE V and Ni concentrations at sites 1 and 3 might be higher, because of their proximity to these sources, than the corresponding concentrations at site 4. Steel mills and blast furnaces make Buffalo similar to Birmingham and Mn, Fe, and Cr might be enriched at all sites in the area. Buffalo receives contributions from air masses passing over the Ohio River Valley where substantial quantities of SO_2 are injected into the atmosphere by power plants (Mueller and Hidy et al, 1981) and can convert to measurable sulfate by the time they reach Buffalo (Kolak et al, 1979). The background site for Buffalo is NYBUB, site 2, which is 30 km south of Buffalo's city center.

The Houston area contains a wide variety of source types. Natural gas combustion is a major source because of its association with petroleum refining, and whereas contributions from this clean-burning fuel will be low in other areas where its use is primarily for domestic heating and cooking, elemental and organic carbon contributions to FINE samples from this source might be significant in Houston. Sampling site 2 is closest to the highly industrialized ship channel and might expect elevated levels of Fe, Mn, and Cr due to the steel foundry. The background reference site 3 is classified as rural residential and though nearby natural gas combustion sources might affect its carbon concentrations, it should serve as a good reference with which to assess the industrial influences on the other sites.

The effect of emissions on the air quality in El Paso cannot be considered independently of the city of Juarez which lies just across the Rio Grande River in Mexico. Emissions in Juarez are not well identified nor quantified so little can be said about them here. Site 1 might be influenced by the nearby smelter (1), though Hubert et al (1981a, 1981b) do not find Pb and As measurements at this site to be enriched (they did not measure Cu or Zn). The steel foundry (3) is too far away to have much influence as are the fluid crackers (5 and 6), concrete batching (7) and rock crushing (2 and 8). The background reference site is in Clint, TX, 45 km southeast of the El Paso city center.

Among all the sites under consideration, Philadelphia has (referring to Table B.2 of Appendix B) the highest population per square mile. Industrial activities are numerous and include mineral handling, residual oil combustion, coal combustion, incinerators, and various metal smelters. Philadelphia is also an important area because of the high concentration of IP sampling sites, special studies and long-term monitoring.

The long-term sampling site 14 at 500 S. Broad is removed from most point sources. It might show enriched FINE concentrations of Pb and Br from local traffic, but few enrichments from industrial sources. Site 11 in a residential area should exhibit elemental concentrations similar to those measured at the background reference site 10, though the mineral handling facilities close to site 11 may cause COARSE Al, Si, Fe, Mn, and Ti to be enriched over the levels at site 10 and the FINE fraction at both sites may be enriched in V and Ni due to the nearby residual oil boilers.

A special neighborhood-scale study was carried out in the Bridesburg industrial area which is shown enlarged in Figure 4.2.8. The Bridesburg area of Philadelphia is a combination of heavy industries, residential and commercial land uses. It covers approximately a 2 km x 4 km area 10 km northeast of the city center. As a special study in EPA's Inhalable Particulate Network, a seven-station, four-month sampling program was carried out in this area. The most interesting effects of sources on receptors are probably to be observed in the Bridesburg area. Grain loading (33) might contribute to COARSE carbon concentrations at site 1 while manganese ore handling (59) and the zinc galvanizing (31, 32) might contribute to sites 1 and 5. The copper and secondary metals smelter (34) may elevate Zn, Pb and Cu concentrations at sites 4, 5 and 6. The coke oven (40) with its associated coal storage piles would most likely elevate FINE and COARSE elemental carbon concentrations at sites 2, 3 and 7. The lead smelter (38) would be expected to raise Pb concentrations at 2, 3 and 7 more than at the other sites. This neighborhood-scale study offers a good opportunity to determine the spatial variability of source contributions to ambient concentrations.

Once again, this examination of individual urban areas is a screening rather than a definitive statement of which sources affect which receptors. Little is known about the operating cycles, control equipment or meteorological conditions prevailing during the times when the airshed was sampled by the IP Network. The value of this screening is in determining which source types need not be further investigated within an urban area. For example, Phoenix, with few industrial sources, presents a much simpler situation than Philadelphia with many and varied industrial sources.

There is value, too, in comparing the source characters and ambient concentrations of different cities with each other. If chemical concentration measurements are similarly enriched between cities with many different source types but with a few in common, then the common types must be causing the enrichments. Similarly, differences in chemical enrichments which correspond to those expected from the different source types will support the hypothesis that those

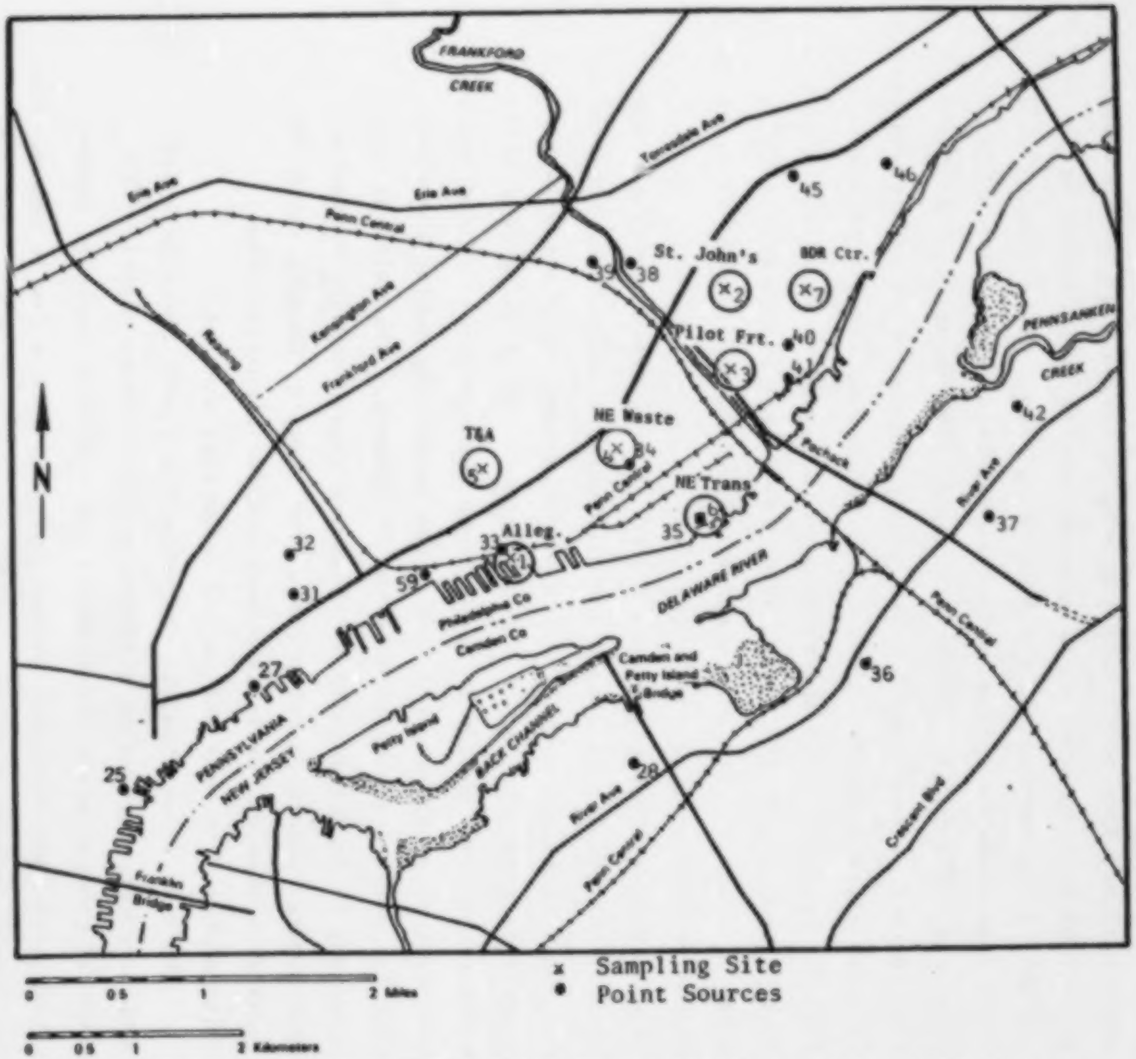

FRANKFORD CREEK
Torresdale Ave
Erie Ave
Erie Ave
Penn Central
Kensington Ave
Frankford Ave
Reading
45
46
St. John's
BDR Ctr.
39
38
2
7
Pilot Frt.
40
3
41
PENNSAUKEN CREEK
42
NE Waste
34
4
T&A
5
N
NE Trans
6
35
Penn Central
Pochack
River Ave
37
Alleg.
33
1
32
31
59
Philadelphia Co
Camden Co
DELAWARE RIVER
Penn Central
27
Camden and Petty Island Bridge
36
PENNSYLVANIA
NEW JERSEY
Petty Island
BACK CHANNEL
25
28
River Ave
Franklin Bridge
Penn Central
Crescent Blvd
0
0.5
1
2 Miles
0
0.5
1
2 Kilometers
x Sampling Site
• Point Sources

Figure 4.2.8 Sampling Site and Point Source Locations in the Bridesburg Industrial Area of Philadelphia. Sites are Identified in Table 4.2.2 and Source Types are Identified in Table 4.2.1.

additional source types do contribute to ambient concentrations of inhalable and fine suspended particulate matter.

The discussion in this chapter results in several observations:

- The urban areas sampled by the IP Network represent a broad coverage of population, meteorological, and emissions cases. Though not all urban areas in the U.S. are represented, the ones that were chosen include major population centers with varying population densities. Major particulate matter sources have been identified and located on maps with respect to IP Network sampling sites in ten of the network urban areas, and seven of these maps were presented in this chapter. Similar maps for other urban areas in the network should be compiled.
- Several of the sites in the IP Network were found to be in proximity to industrial sources which emit chemical species measured on IP Network samples. If these sources are contributors to suspended particulate matter concentrations, the concentrations of chemical species which they emit should be elevated above those at more distant sampling sites. This analysis is done in Chapter 9 of this report.
- Some of the sources located in this document may not have been in operation during IP Network sampling. The National Emissions Data System is a useful adjunct to the IP Network. Many of the entries are dated, however, and the report formats are not convenient for the receptor-oriented assessments of particulate matter concentrations, so considerable effort is required to extract information from it.

CHAPTER 5

GEOGRAPHICAL AND SEASONAL VARIABILITY OF TSP, IP, AND FP IN URBAN AREAS

The spatial and temporal distributions of the size-classified samples acquired in the IP Network can provide information on a number of issues related to TSP, IP and FP concentrations:

- Standard Attainment: The IP Network is research oriented rather than compliance oriented, and the measurements obtained from it are not intended for testing an area's attainment of a standard. However, the distribution of average and maximum concentrations provides an estimate of which areas are most likely to be in or out of compliance with a standard and can serve as a preview of that which routine compliance monitoring might eventually find.

- Causes of Elevated and Depressed Concentrations: The variation of concentrations with meteorological subregions, urban emissions and time of year provides a basis for speculation on causes of observed particulate matter measurements which can be supported or refuted by further study.

- Sampler Spacing: The spatial variability of ambient concentrations within an area allows an estimate to be made of the density of samplers required to truly represent the pollutant concentrations in that area.

- Sampling Schedule: Different seasons of the year are influenced by different meteorological and emissions conditions. An annual average will be affected by the frequency of samples taken within each season if the seasonal averages differ substantially.

The seasonal and annual averages drawn from urban sampling sites are presented and examined in this chapter to address these issues.

5.1 TSP, IP and FP Urban Concentrations

Data collected by the IP Network present several opportunities for the examination of spatial distributions of TSP, IP and FP on regional, urban and neighborhood scales. The network's widespread geographical location of samplers allows concentrations from various urban areas in the United States to be compared and regional patterns to be discerned. Availability of a complete year of data from two or more sites in the environs of Birmingham, AL, Los Angeles, CA, San Francisco, CA, Buffalo, NY and Philadelphia, PA provides insight into urban scale spatial distributions of particulate matter. The special study of the Bridesburg Industrial area of Philadelphia provides similar insight into spatial distributions on the neighborhood scale.

Table 5.1.1 contains the arithmetic average concentrations of TSP, IP and FP at sites in the IP Network for a full year of monitoring beginning on October 1, 1979 and ending on September 30, 1980. The IP and FP concentrations correspond to the TOTAL and FINE measurements at the sites. At the time of this writing, SSI measurements of IP were much less complete than the TOTAL measurements of IP. Each quarter's values have been averaged separately to reveal the seasonal distribution. Only averages containing more than five values have been included. The annual arithmetic average was calculated as the average of the four quarterly averages rather than from the entire set of data for that year. Early in the network operations, many samples were lost due to start-up problems, resulting in a nonuniform distribution of samples between quarters. This averaging procedure gives each season equal weight in determining the annual mean, regardless of the number of samples acquired.

Table 5.1.2 contains the maximum concentrations of TSP, IP and FP found during each season. Only maxima from quarters with more than five TSP, IP and FP values are listed. The annual maxima are the highest values which occurred in any one of these quarters. The data in this table were taken from summary reports produced by EPA/EMSL and were not screened by the procedure of inequalities 3-1 to 3-4.

5.2 Regional Geographical Distributions

The urban areas have been grouped by five geographic regions of the country. At those sites for which annual arithmetic averages were calculated, the highest average IP concentrations were found in Los Angeles (92 ug/m^3), El Paso (68 ug/m^3), Buffalo (63 ug/m^3) and Birmingham (58 ug/m^3). There is no clear regional pattern but a wide variability in concentrations between urban areas is seen.

The average of FP at urban sites ranges from 13 ug/m^3 in San Francisco (Richmond) to 37 ug/m^3 in Los Angeles. The regional

TABLE 5.1.1

QUARTERLY AND ANNUAL ARITHMETIC AVERAGES OF TSP, IP AND FP IN URBAN AREAS AT THIRTY-EIGHT NETWORK SITES

(IP and FP are from Dichotomous Sampler Measurements)

IP Urban Site	Fall, 1979 (ug/m^3)	Winter, 1980 (ug/m^3)	Spring, 1980 (ug/m^3)	Summer, 1980 (ug/m^3)	4-Season Average (ug/m^3)
Northeast					
Hartford, CT					
Hartford	53/41/22[a]	62/34/16	69/41/25		
Washington, D.C.					
Washington	59/36/23	66/42/27	84/33/19		
Pittsburgh, PA					
Hazelwood	-/68/37	-/59/34			
Philadelphia, PA					
500 S. Broad	57/44/26	53/ -/ -	70/42/22		
Allegheny	106/58/24	128/61/25			
N.E. Airport	42/34/24	35/33/21	53/35/19	65/45/28	49/37/23
Pres. Home	48/43/28	43/51/39	62/48/28	76/50/31	57/48/32
St. John's	59/53/33	55/42/26			
Baltimore, MD					
Baltimore		-/48/27			
Boston, MA					
Boston		62/35/20		83/49/31	
E. Boston		44/33/19	61/32/16	65/41/26	
Buffalo, NY					
P.S. 26	63/56/29	82/72/33	98/62/31	104/60/40	87/63/33
P.S. 28	78/50/24	92/51/27	114/53/28	109/53/28	98/52/27
Wilmuth		133/40/23			
Midwest					
Minneapolis, MN					
Minneapolis A	33/25/14	44/30/18	72/37/14	55/27/11	51/30/14
Minneapolis B	53/37/16	65/43/23	91/45/15	94/44/15	76/52/17
St. Louis, MO					
Affton		63/31/21	90/40/19	79/59/27	
Akron, OH					
Morley Health	61/42/23	62/49/27	80/47/23	81/56/32	71/43/26
Cincinnati, OH					
Cincinnati	48/33/22	42/40/26	59/39/22	68/51/37	54/41/27

TABLE 5.1.1 (Continued)

IP Urban Site	Fall, 1979 (ug/m^3)	Winter, 1980 (ug/m^3)	Spring, 1980 (ug/m^3)	Summer, 1980 (ug/m^3)	4-Season Average (ug/m^3)
Midwest					
Steubenville, OH					
Washington Sch.	113/71/45	99/58/38			
Kansas City					
Kansas		86/45/34	111/52/29	114/56/19	
Missouri		97/54/25	109/58/19	90/46/15	
South					
Birmingham, AL					
S. Birmingham	52/35/21	40/30/18	75/49/28	83/46/29	63/40/24
N. Birmingham	88/36/26			150/80/37	
Inglenook	103/43/26	87/44/19	136/68/28	120/63/31	112/55/26
Mtn. Brook	-/28/15	36/23/15	58/33/21	64/34/24	-/30/19
Tarrant City	83/40/28	91/35/21	133/79/43	148/78/34	114/58/32
Dallas, TX					
Dallas		114/37/26	76/32/22	74/39/16	
Southwest					
El Paso, TX					
Tillman	155/92/31	103/ -/ -	111/67/30	108/46/12	125/68/26b
West Coast					
Los Angeles, CA					
Azusa	115/68/30	77/38/16			
West LA	77/60/36	68/38/21	77/43/18	68/42/23	73/46/25
Pasadena	98/74/40	35/41/24			
Rubidoux	163/106/48	72/47/17	136/96/39	206/119/42	161/92/37
San Francisco, CA					
Livermore	-/60/15	50/40/18	63/28/10	-/42/15	
Richmond	48/30/17	46/31/21	53/21/07	47/17/07	49/25/13
S.F. East		64/44/29		45/23/09	
San Jose	93/47/24	73/39/23	64/24/09	85/31/14	79/35/18
Seattle, WA					
Seattle Light	41/24/14	41/28/18	36/20/09	39/23/11	39/24/14
All Sites (with four quarters of data)					80/46/24

[a] Format is TSP/IP/FP.

[b] Average of three quarters data.

TABLE 5.1.2

QUARTERLY AND ANNUAL MAXIMA OF TSP, IP AND FP IN URBAN AREAS AT THIRTY-EIGHT NETWORK SITES

(IP and FP are from Dichotomous Sampler Measurements)

IP Urban Site	Fall, 1979 (ug/m^3)	Winter, 1980 (ug/m^3)	Spring, 1980 (ug/m^3)	Summer, 1980 (ug/m^3)	4-Season Average (ug/m^3)
Northeast					
Hartford, CT					
Hartford		131/103/59[a]	93/53/33	95/68/44	
Washington, D.C.					
Washington	126/86/48	90/85/72	128/59/35		
Pittsburgh, PA					
Hazelwood	-/154/79	-/85/48			
Philadelphia, PA					
500 S. Broad	179/117/69	96/ -/ -	123/78//39		
Allegheny	200/134/82	226/113/49			
N.E. Airport	113/134/90	77/70/47	84/60/37	137/134/99	137/134/99
Pres. Home	161/146/112	73/ -/ -	94/37/43	149/113/88	161/146/112
St. John's	200/149/101	98/64/42			
Baltimore, MD					
Baltimore		-/94/50			
Boston, MA					
Boston		93/54/41		102/76/55	
E. Boston		81/69/47	80/40/21	97/65/49	
Buffalo, NY					
P.S. 26	122/114/55	165/134/56	160/110/56	150/95/70	165/134/70
P.S. 28	144/80/38	152/111/54	191/94/47	163/95/58	191/111/58
Wilmuth		222/122/35			
Midwest					
Minneapolis, MN					
Minneapolis A	62/42/27	98/55/44	126/61/21	85/49/21	126/61/44
Minneapolis B	98/55/29	99/63/47	183/82/22	221/105/31	221/105/47
St. Louis, MO					
Afton		94/56/39	137/63/40	118/85/48	
Akron, OH					
Morley Health	109/84/47	121/95/48	117/77/43	114/81/55	121/95/55
Cincinnati, OH					
Cincinnati	88/69/47	68/64/45	114/64/37	121/83/73	121/83/73

TABLE 5.1.2 (Continued)

IP Urban Site	Fall, 1979 (ug/m^3)	Winter, 1980 (ug/m^3)	Spring, 1980 (ug/m^3)	Summer, 1980 (ug/m^3)	4-Season Average (ug/m^3)
Steubenville, OH					
Washngton Sch.	223/134/85	192/129/64			
Kansas City					
Kansas		114/60/50	168/72/48	179/90/33	
Missouri		155/67/44	160/92/34	117/77/56	
South					
Birmingham, AL					
S. Birmingham	73/56/35	60/45/30	110/75/48	120/68/46/	120/75/48
N. Birmingham	192/79/50			237/134/55	
Inglenook	313/102/52	176/71/30	299/140/41	177/90/45	313/140/52
Mtn. Brook	-/65/24	59/32/25	82/46/36	91/55/37	-/65/37
Tarrant City	145/79/48	190/68/38	174/89/42	211/110/49	211/110/49
Dallas, TX					
Dallas		474/88/62	111/60/46	90/58/33	
Southwest					
El Paso, TX					
Tillman	320/213/61	227/ -/ -	208/93/24	211/86/23	320/-/-
West Coast					
Los Angeles, CA					
Azusa	168/115/69	125/62/29			
West LA	146/99/72	97/80/60	113/66/30	125/80/58	146/99/72
Pasadena	169/118/76	-/78/84			
Rubidoux	250/171/109	181/99/52	231/156/60	392/200/106	392/200/109
San Francisco, CA					
Livermore	-/139/34	81/72/50	95/47/16	103/87/60	103/87/60
Richmond	102/51/39	69/81/71	73/29/10	85/41/13	102/81/71
S.F. East		101/84/59		121/64/28	
San Jose	269/106/78	139/113/82	82/40/15	129/51/23	269/113/82
Seattle, WA					
Seattle Light	90/58/51	71/51/34	74/38/17	56/32/24	90/58/51
All Sites (for sites with more than 5 samples/quarter for four quarters)					392/200/112

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[a] Format is TSP/IP/FP.

distribution of these annual averages is fairly homogeneous in the eastern United States, ranging from 22 ug/m^3 in Birmingham to 32 ug/m^3 in Philadelphia. Average FP concentrations west of the Mississippi River are generally lower, with the exception of El Paso and Los Angeles.

Maximum 24-hr concentrations of IP vary substantially and rarely occur on the same day at nearby sites. They appear to be more affected by local than by regional phenomena. The spatial variability of these maxima in the West seems comparable to the spatial variability in the East. These maxima range from 58 ug/m^3 in Seattle (Seattle Light) to 200 ug/m^3 in Los Angeles (Rubidoux). These measured maxima might be larger if sampling were undertaken daily rather than every sixth day. This subject is examined in Chapter 7.

FP annual maxima range from 44 ug/m^3 at Minneapolis (site A) to 112 ug/m^3 at Presbyterian Home in Philadelphia. The variability within regions of the U.S. is comparable to the variability between regions.

Thus, with respect to a standard which might be formulated in terms of an annual average and a 24-hr maximum, all sites would be in compliance if an IP standard specified a 92 ug/m^3 annual average and a 213 ug/m^3 maximum and if an FP standard required concentrations less than a 37 ug/m^3 annual average and a 112 ug/m^3 maximum. For lower values, the number of potential non-compliance sites could be evaluated by selecting those with averages and maxima greater than the standard from Table 5.1.1.

The urban areas with the highest IP average concentrations are Los Angeles (92 ug/m^3), Birmingham (58 and 55 ug/m^3), El Paso (Texas has a rule for invalidating TSP samples collected during duststorms which has not been applied to IP Network data. Thus, the IP average of 68 ug/m^3 and maximum of 213 ug/m^3 may be biased if duststorms occurred) and Buffalo (63 and 52 ug/m^3). Of all the sites evaluated, these same urban areas exhibit the highest 24-hr IP concentrations (maxima are 134 and 111 ug/m^3 in Buffalo, 140 and 110 ug/m^3 in Birmingham, 99 and 200 ug/m^3 in Los Angeles). San Jose (113 ug/m^3) and Philadelphia (134 and 146 ug/m^3) also show high 24-hr maximum concentrations. For the most part, the remaining urban areas exhibit average IP concentrations of less than 50 ug/m^3 and maximum concentrations of less than 100 ug/m^3.

The IP Network was never intended to measure compliance. A network oriented toward monitoring compliance with a standard might find higher or lower annual average and maximum concentrations than those cited here depending on sampler locations and sampling frequencies.

5.3 Urban Geographical Distributions

The ranges of TSP, IP and FP annual average concentrations and maximum concentrations within urban areas having two or more sampling sites are presented in Table 5.3.1. The range of values for all sites appears in the last row of the table. The variability of both averages and maxima between different sites within each area is evident from these ranges. In no case can data from a single sampler be said to spatially represent the urban area with reasonable precision. Even for FP, which shows the smallest range of values, the minimum ratio of the high average to the low average occurs for the Buffalo area at 1.22. This implies that if only the P.S. 28 sampling site were used to represent the entire Buffalo area, then average FP concentrations at P.S. 26 would be underestimated by 22%. The relative differences between spatially separated averages within the same geographical area are higher for other urban areas and size fractions. For example, if the West LA IP average were used to represent the average IP concentration at Rubidoux, the estimate would be incorrect by 100%.

Similarly, maximum concentrations vary from site to site within an urban area. The minimum ratio of FP maxima is in Philadelphia, where the ratio is 1.13, but in other areas this ratio is substantially higher. Once again, in Los Angeles the IP maximum in Rubidoux is twice that of West LA.

The variability among sites within a single urban area does appear to be less than the variability of all the urban areas sampled, though it may be unfair to infer this because the 19 sites of the

TABLE 5.3.1

RANGES OF TSP, IP AND FP

ANNUAL ARITHMETIC AVERAGE AND MAXIMUM CONCENTRATIONS

BETWEEN SITES WITHIN URBAN AREAS

Urban Area	No. of Sites	TSP, ug/m^3 Average	TSP, ug/m^3 Maximum	IP, ug/m^3 Average	IP, ug/m^3 Maximum	FP, ug/m^3 Average	FP, ug/m^3 Maximum
Birmingham	4	63 to 114	120 to 313	30 to 58	75 to 140	19 to 32	37 to 52
San Francisco	3	49 to 79	103 to 269	25 to 35	81 to 113	13 to 18	60 to 82
Buffalo	2	87 to 98	165 to 191	52 to 63	111 to 134	27 to 33	58 to 70
Los Angeles	2	73 to 161	146 to 392	46 to 92	99 to 200	25 to 37	72 to 109
Philadelphia	2	49 to 57	137 to 161	37 to 48	134 to 146	23 to 32	99 to 112
Minneapolis	2	51 to 76	126 to 221	30 to 42	61 to 105	14 to 17	44 to 47
All Sites	19	39 to 161	90 to 392	24 to 92	58 to 200	13 to 37	44 to 112

combined data represent a considerably larger population to draw from than the 2 or 3 sites in a single urban area; if each urban area had averages and maxima from a larger number of sites, the comparison would be fairer. Still, the range over all sites is large. For averages, the ratios of maximum to minimum are 4.1 for TSP, 3.8 for IP and 2.8 for FP. For maxima, these ratios are 4.4 for TSP, 3.4 for IP and 2.5 for FP. The ratios of these overall range limits are significantly higher than the corresponding ratios within an individual urban area.

It is evident that the monitoring of urban concentrations of TSP, IP and FP will require at least an urban-scale (see Table 3.1.1) monitoring network to adequately represent the spatial distribution of these concentrations. In certain situations, a smaller scale, a neighborhood scale, of sampler spacing may be required to adequately represent an area.

5.4 Neighborhood Geographical Distributions

To understand more fully the spatial patterns within and around a heavily industrialized area, the Bridesburg industrial area of Philadelphia was the subject of an intensive sampling effort from October 3, 1979 to February 15, 1980. Seven sampling sites were located within a 2 km x 4 km area. Three sites were within the Bridesburg industrial area and four other sites were on its perimeter. These are shown in relation to each other and nearby industrial sources as sites 1 to 7 in Figure 4.2.8. Sites 1, 3 and 4 are the core sites and sites 2, 5, 6 and 7 are the perimeter sites. An urban background site, NE Airport, was located approximately 10 km away to the northeast at a small airport in a less densely populated area in a generally downwind direction. This is site 10 in Figure 4.2.7.

Figure 5.4.1 compares the average and range of concentrations of TSP, IP and FP within the core, perimeter and NE Airport subgroupings as a function of distance from the industrial area. The data used for this figure did not go through the screening process of inequalities 3-1 to 3-4. The ranges show substantial variability within each

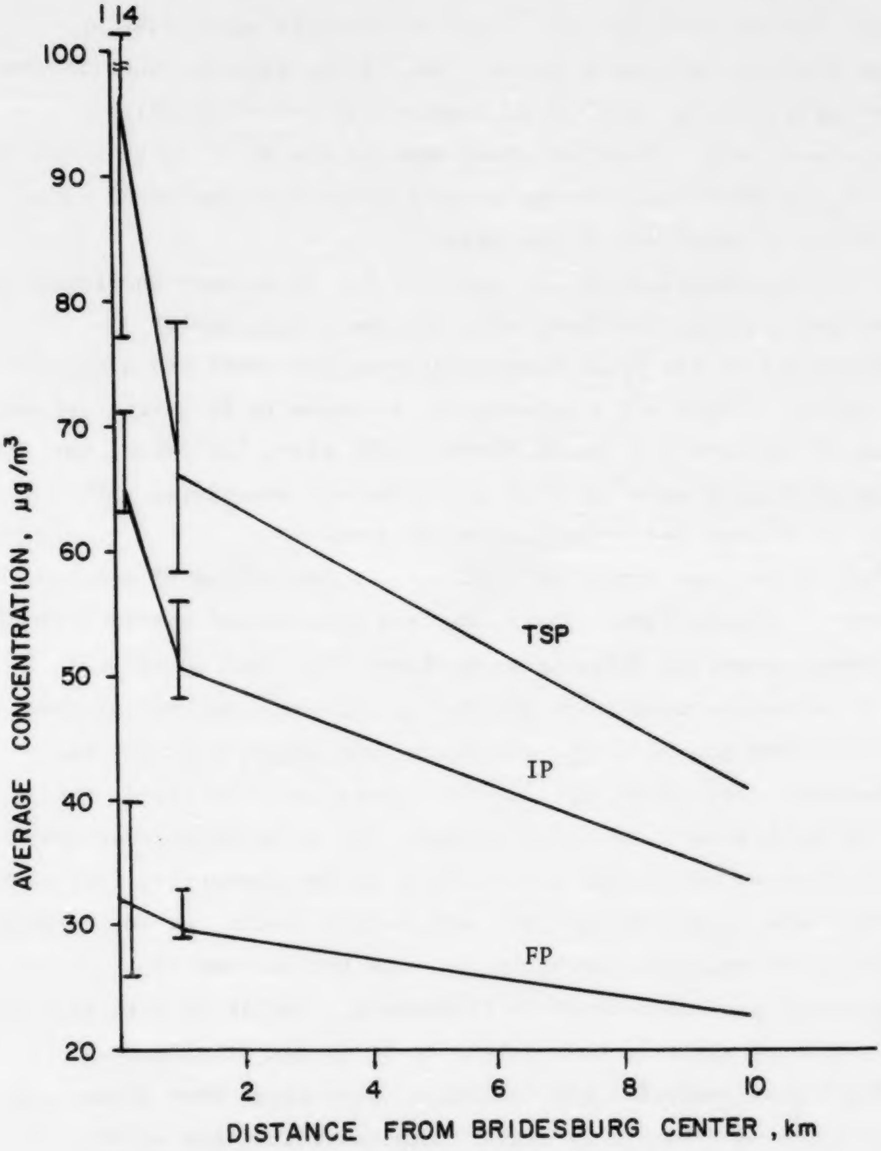

Figure 5.4.1 Average Concentrations and Concentration Ranges in Bridesburg Area Versus Distance Between Sites for TSP, IP and FP

classification, but there are major differences between the core, perimeter and airport groupings.

TSP and IP are 45%, and 31% higher at core sites when compared to perimeter sites. Absolute concentration differences are 30 ug/m^3 for TSP, and 16 ug/m^3 for IP. These differences occur over an average distance between sites of 1 km. It is apparent that TSP and IP concentrations are not homogeneously distributed on this neighborhood scale. From the study area to the NE Airport, a distance of 10 km, an additional average concentration decrease of 25 ug/m^3 for TSP and 17 ug/m^3 for IP was seen.

A similar decrease was not observed for FP between the industrial and perimeter sites. In fact, with one exception, the FP concentrations in the Bridesburg study area all exhibited a rather flat profile. There was a substantial decrease in FP levels between the industrial area and the NE Airport (10) site, indicating that an average of 8 to 10 ug/m^3 of fine particles was associated with sources in or near the industrial study area.

This poses some important problems for the siting of monitors to represent a neighborhood. These samplers were spaced within 1 km of each other, a spacing which is much closer than that which would be found in a routine compliance monitoring network. Any one of them could have been chosen as the compliance monitoring site for the neighborhood. Yet, given appropriate values for a standard, this area could be in attainment or non-attainment depending on whether the monitor selected was in the perimeter or in the industrial core area.

This case is an extreme one; most neighborhoods are not so highly industrialized and would probably not show the extreme IP concentration gradients found in Bridesburg. Yet it is just this type of neighborhood which is most likely to be in non-attainment.

Since both perimeter and industrial core sites show IP and TSP concentrations substantially higher than concentrations at the background site, the incremental amounts must be due to sources of particulate matter originating in the neighborhood. Speculations on what those sources might be were advanced in Chapter 4. In Chapter 9 a receptor model approach will be applied to further identify likely contributors to the observed concentrations.

The problem of siting a single sampler to represent an entire area still remains, however, and development of a method to perform such siting for compliance monitoring program will be just as important as the formulation of a new standard when it comes to determining attainment status.

5.5 Seasonal Distributions

The IP Network offers the opportunity to evaluate seasonal patterns in various urban areas and regions of the country. All samples are of 24-hr duration, which precludes examination of the hourly variability, and the sixth day sampling schedule (third day at some sites) does not provide a strong data base for investigating daily distributions or weekday/weekend patterns. The seasonal averages presented in Table 5.1.1 do allow variability between seasons to be assessed.

Seasonal patterns of average and maximum IP and FP concentrations are examined by reading across a row of Table 5.1.1 or 5.1.2 for a specific sampling site. Trijonis et al (1980), studied the St. Louis regional monitoring data and concluded that IP and FP concentrations peak in the summertime. This hypotheses can now be evaluated in other parts of the country.

Figure 5.5.1a shows the seasonal variation in average quarterly concentrations for IP and FP in 11 eastern and midwestern cities. This geographical subset of sites was selected because of the regional patterns shown above for FP concentrations. There is a slight increase in FP in the summer, which causes IP to be higher, although the increase is only 7 ug/m^3 over the fall-winter-spring averages. The ranges appear to be generally similar among the quarters, except that FP seems less variable in both spring and fall. Figure 5.5.1b shows the seasonal variation of quarterly maxima. FP is seen to be lower in the spring. The CP fraction can be observed in these figures as the difference in FP and IP levels. It is interesting that in the spring the FP/CP ratio is lower than in the other seasons, suggesting a different mix of sources of IP in the spring.

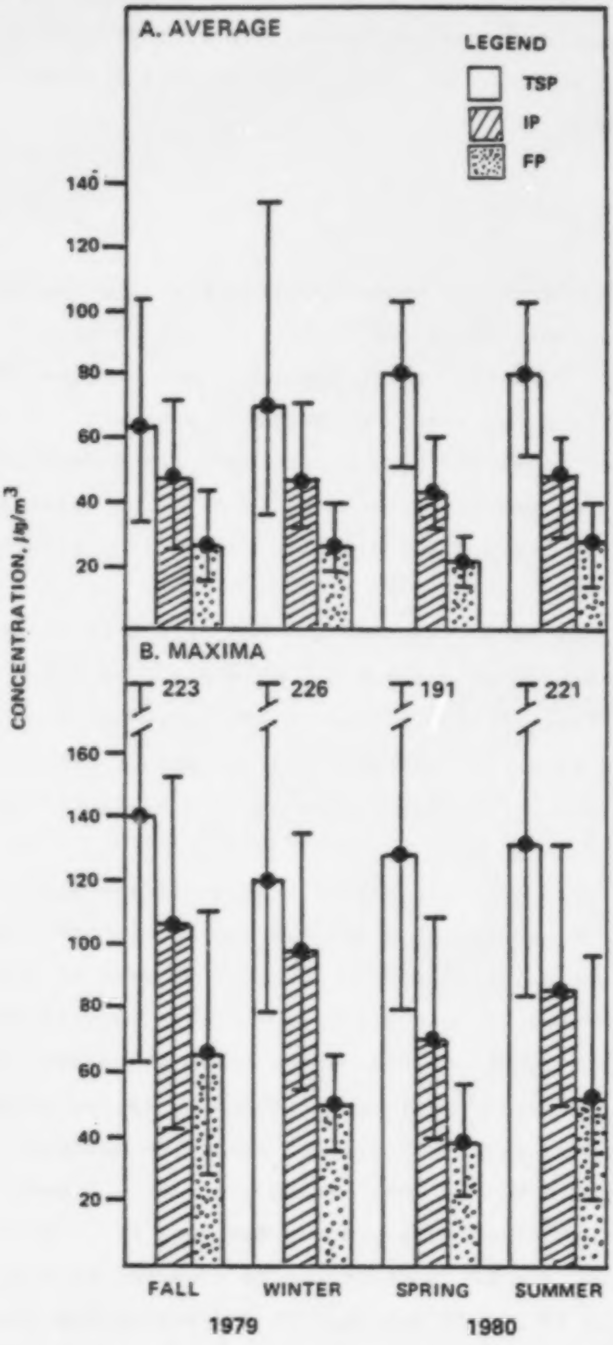

Figure 5.5.1a-b Seasonal Variation of Quarterly TSP, IP and FP Averages(a) and Maxima(b) in 11 Eastern and Midwestern U.S. Urban Areas

The data suggest that FP might be slightly lower in the spring season and higher in the summer, causing IP to be slightly higher in the summer. However, there is not sufficient evidence to suggest that there is a general seasonal pattern in IP and FP similar to that shown in St. Louis.

It is evident that though there may be specific areas in which seasonal differences are unimportant, enough variability exists between seasons to require sampling on an annual basis, with approximately equal numbers of samples taken in each season.

The temporal and spatial coverage of the data available for this report severly limits the certainty with which conclusions can be drawn about the attainment of standards, causes of elevated and depressed concentrations, sampler spacing and sampling schedules. The following observations about these issues based on the preceding discussion must be considered tentative; their applicability will be greater when a similar analysis is applied to the more complete IP Network measurements in the future.

- Annual arithmetic averages of IP and FP can exceed 90 ug/m^3 and 35 ug/m^3, respectively, in urban areas, though the typical average concentrations appear to be approximately 50 ug/m^3 and 25 ug/m^3, respectively. Primary standards for annual IP averages in the 55 to 120 ug/m^3 range (Hileman, 1981) would find most, and possibly all, of the sites examined here in compliance. This range is tentative and may have been modified subsequent to the writing of this report.

- Annual 24-hr maximum concentrations of IP and FP can exceed 200 ug/m^3 and 100 ug/m^3, respectively, in urban areas. Typical values are approximately 100 ug/m^3 for IP and 60 ug/m^3 for FP. Hileman (1981) cites a 24-hr maximum IP range of 150 to 350 ug/m^3 for a primary standard and a 24-hr maximum FP range of 70 to 220 ug/m^3 for a secondary standard. Once again, most, if not all IP Network sites would be in compliance with such a standard. The values cited by Hileman (1981) are tentative and the form and values of a 24-hr standard may have been modified subsequent to the writing of this report.

- The urban and neighborhood scale IP and FP measurements vary significantly from site to site within the areas studied. The implications are that 1) local (within a few kilometers of the sampler) sources are significant contributors to IP concentrations and 2) present spacing between sampling sites may be inadequate to fully represent IP concentrations in certain urban areas and neighborhoods. Methods of determining the sampling uncertainty due to sampler placement should be developed and applied.

- Seasonal averages of IP and FP tend to peak slightly in the summer periods, but there are many individual exceptions at IP Network sites. This conclusion is speculative because of the inadequate seasonal data available for this report. If the conclusion is valid then sampling should take place on a yearly basis for the determination of long-term averages so that all seasons are equally weighted. A seasonally weighted annual average might be a more appropriate method of calculating the annual average if the number of samples in one or more seasons differs by a large amount from the number of samples taken in another season.

CHAPTER 6

GEOGRAPHICAL AND SEASONAL VARIABILITY OF TSP, IP AND FP IN NON-URBAN AREAS

While the geographical and seasonal distributions of suspended particulate matter at the urban sites showed the potential of certain urban areas to exceed a size-classified standard, an examination of the geographical and seasonal variability of non-urban concentrations assists in estimating that portion of an urban average or maximum concentration which is not subject to control of emissions within the urban area.

These non-urban measurements are particularly useful when they are from the same air masses that affect nearby urban areas but which are not significantly influenced by the emissions from those areas. The roles of synoptic weather conditions covering broad geographic scales and of long-range transport from one urban or industrial area to another are better defined when the variability of ambient concentrations due to local emissions is removed.

No site within the United States, and possibly even the world, will be completely free of anthropogenic contributions to its ambient aerosol. Yet, from the practical standpoint of a localized urban area, it is sufficient to separate that which is transported into the area from that which originates in the urban area, regardless of the origins of the transported material. Regional-scale studies must then be undertaken to separate the natural from anthropogenic contributions at non-urban sites. In this chapter, regional-scale measurements from the IP Network and from the SURE Network are tabulated, examined, and compared data from nearby urban sites.

6.1 TSP, IP and FP Non-Urban Concentrations

Several sites in the IP Network are removed enough from populated areas that they can be considered non-urban, even though in some cases they may be influenced by nearby urban areas. Eight of these sites had acquired a large enough number of measurements by the time of this writing to determine seasonal averages and maximum concentrations for TSP, IP and FP. As in Chapter 5, only quarterly periods with more

than 5 measurements were examined and the values were taken from IP Network data summaries produced by EPA/EMSL that did not go through the data filtering of inequalities 3-1 to 3-4. IP and FP correspond to the TOTAL and FINE measurements of the dichotomous sampler. The averages at these sites appear in Table 6.1.1 and the maximum concentrations are presented in Table 6.1.2. The annual averages in Table 6.1.1 were calculated as the average of the four seasonal averages to remove any bias caused by an unequal number of samples per season. As for the urban concentrations in Tables 5.1.1 and 5.1.2, the non-urban sites have been grouped by regions of the United States. At the bottom of each seasonal column, averages of the averages from each site have been recorded as indicators of the overall non-urban concentration average. A similar set of numbers appears in Tables 5.1.1 and 5.1.2 for urban measurements.
Figure 3.1.1 shows where these non-urban sites are located in relation to the urban areas sampled by the IP Network.

Measurements in the eastern United States can be supplemented by TSP, IP and FP measurements from the SURE (Perhac, 1978, Mueller et al, 1980, Miller, 1981, Perhac et al, 1981) which were taken during 6 seasonally representative month-long periods from August, 1977 to October, 1978. Figure 6.1.1 shows the locations of the 9 SURE Class I sampling sites which are identified in Table 6.1.3. Detailed descriptions of these sites, the measurements made and the regional-scale interpretations drawn from them are to be presented in Mueller and Hidy et al (1981). The comparison of the SURE and IP Network sampling inlets in Chapter 2 showed that the IP fraction of the total aerosol mass collected by the SURE sampler is within 10% to 20% of the IP fraction collected by the IP Network samplers. The FP fractions collected by both samplers were shown to be identical.

SURE aerosol samples were taken on Teflon coated glass fiber filters which were specially chosen to be free of sulfate artifacts, and though a nitric acid artifact was found, it was much less than that of the standard glass fiber filters. Arithmetic averages of TSP at each site for each of the seasonal months were calculated from all the valid, 24-hr samples available for that month; the arithmetic averages reported here differ from the geometric averages calculated

TABLE 6.1.1

QUARTERLY AND ANNUAL ARITHMETIC AVERAGES OF TSP, IP AND FP IN U.S. NON-URBAN AREAS AT EIGHT IP NETWORK SITES

IP Non-Urban Site	Fall, 1979 (ug/m^3)	Winter, 1980 (ug/m^3)	Spring, 1980 (ug/m^3)	Summer, 1980 (ug/m^3)	4 Season Average (ug/m^3)
West					
Pearl City, HA	30/14/8[a]	37/22/14	30/16/7	34/13/5	33/16/9
Winemucca, NV	39/33/8	30/23/5	50/28/5	105/-/-	56/28/6
Sauvie Island, OR	24/31/16	22/-/19	47/37/9	56/30/14	37/33/15
Clint, TX	100/68/12	76/51/10	106/74/15	71/44/13	88/59/13
Average for Western Sites	48/37/11	41/32/12	58/39/12	67/29/11	54/34/11
East					
Braidwood, IL	36/30/15	37/40/27	80/34/22	66/32/16	55/34/20
RTP, NC	30/26/22	29/10/17	50/23/17	60/43/37	42/28/23
Seabrook, TX	49/42/16	34/28/14	52/33/12	60/34/16	49/34/15
Big Sister Sewage, NY	25/21/17	29/19/14	44/24/18	55/-/-	38/21/16
Average at Eastern Sites	35/30/18	32/27/18	57/29/17	60/36/23	46/29/19
Average for all Sites	42/34/15	37/30/15	57/34/15	63/33/17	50/32/15

[a] Format is TSP/IP/FP.

TABLE 6.1.2

QUARTERLY AND ANNUAL MAXIMA OF TSP, IP AND FP AT EIGHT IP NETWORK SITES

IP Non-Urban Site	Fall, 1979 (ug/m^3)	Winter, 1980 (ug/m^3)	Spring, 1980 (ug/m^3)	Summer, 1980 (ug/m^3)	4 Season Average (ug/m^3)
West					
Pearl City, HI	38/ 21/14[a]	57/ 56/55	46/ 47/21	39/16/ 7	57/ 56/55
Winemucca, NV	59/ 60/11	48/ 43/ 7	88/ 56/ 9	180/ -/ -	180/ 60/11
Sauvie Island, OR	59/ 68/43	48/ -/34	170/ 77/16	114/65/39	170/ 77/43
Clint, TX	218/131/17	210/116/23	240/171/29	124/73/20	240/171/29
Maxima of Western Sites	218/131/43	210/116/55	240/171/29	180/73/39	240/171/55
East					
Braidwood, IL	101/ 69/39	88/ 78/57	161/ 69/34	153/57/28	161/ 78/57
RTP, NC	47/ 36/31	45/ 31/29	74/ 37/29	83/41/31	83/ 41/31
Seabrook, TX	70/ 52/21	54/ 50/38	63/ 41/20	87/65/43	87/ 65/43
Big Sister Sewage, NY	48/ 51/43	68/ 37/24	73/ 49/34	85/ -/ -	85/ 51/43
Maxima of Eastern Sites	101/ 69/43	88/ 78/57	161/ 69/34	153/ 65/43	161/ 78/57
Maxima of All Sites	218/131/43	210/116/57	240/171/34	180/ 73/43	240/171/55

[a] Format is TSP/IP/FP.

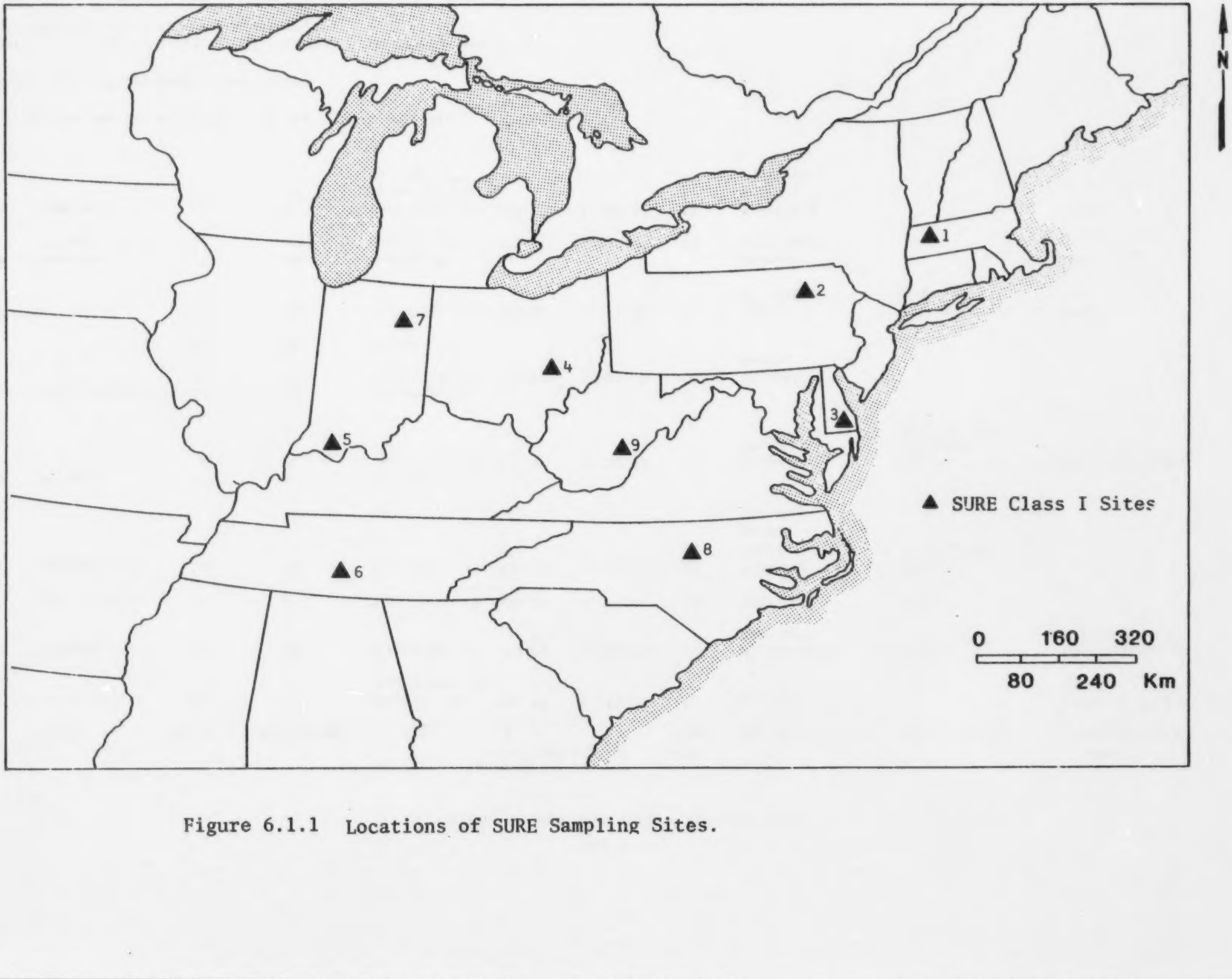
N
1
2
3
4
5
6
7
8
9
▲ SURE Class I Sites
0
80
160
240
320
Km

Figure 6.1.1 Locations of SURE Sampling Sites.

TABLE 6.1.3

LOCATIONS OF NINE SURE CLASS I SAMPLING SITES

Station No.	Station Name	Miles	Direction[a]	City	Location of Site UTM Coordinates X	Location of Site UTM Coordinates Y	UTM Zone	Map Ref.[b]	Local Sources[c]	Existing Measurements
01	Montague	15 5	N SE	Amherst, MA Greenfield, MA	702.88	4,715.55	18	Albany		WD/WS at 5 level on Tower
02	Scranton	25	NW	Scranton, PA	410.64	4,604.80	18	Williamsport Scranton	P1SE	SO_2, TSPm WD.WS 3 levels on Tower
03	Indian River	1	E	Millsboro, DE	476.16	4,270.48	18	Salisbury	P.5N	
04	Duncan Falls	8	SE	Znesville, OH	424.30	4,411.39	17	Clarsburg Canton Marion Columbus	Ferro Alloy 3.2NE	
05	Rockport	0.5 8	W N	Rockport, KY Owensboro, KY	494.80	4,192.40	16	Evansville Vincennes	P8.5S, P13.5WNW, Recycle 5NE	Met Tower 6 NNE
06	Giles County	24 42 10	SSE NW NE	Columbia, TN Huntsville, AL Pulaski, TN	508.90	3,904.48	16	Columbia Gasden		
07	Ft. Wayne	15	SW	Ft. Wayne, IN	639.05	4,535.65	16	Muncie Ft. Wayne	Quarry (sand) 1.5 NE	None
08	Research Triangle Park	7 10	SE NW	Durham, NC Raleigh, NC	695.54	3,973.00	17	Raleigh Greensboro		None
09	Lewisburg	5 2	E SW	Lewisburg, WV White Sulfur Springs, WV	558.72	4,180.80	17	Bluefield Roanoke Charleston		None

[a] Directions are the direction from the city to the site.

[b] USGS 1:250,000 topographic map series.

[c] Refer to Mueller and Hidy et al. (1981) for detailed descriptions and possible local source influences.

by Mueller and Hidy et al (1981). Eight IP and FP samples of 3-hr duration were taken each day. SURE data summaries report monthly averages for each 3-hr period; the average of these averages was used to represent the monthly average. This would be equivalent to the monthly average of all 3-hr samples if no samples were missing; since few months experienced 100% data captures, there may be slight differences between the averages reported here and those calculated by other methods. Table 6.1.4 contains the results of these calculations. The fifteen-month averages for each site are the averages of the averages from the six seasonally representative months.

The maximum 24-hr TSP, IP and FP concentrations during each month of sampling at each site were selected from the SURE data summaries and are tabulated in Table 6.1.5. For the 3-hr duration IP and FP samples, only days with 6 or more valid samples were considered. The averages of the 3-hr samples for the two or three days on which the highest 3-hr concentrations occurred were calculated and the highest of these averages was taken to be the maximum for that month.

With the data in Tables 6.1.1, 6.1.2, 6.1.4 and 6.1.5, it is possible to observe the regional and seasonal distributions of TSP, IP and FP concentrations for non-urban areas, analogous to the examination of urban concentrations presented in Chapter 5, and to compare urban to non-urban concentrations.

6.2 Regional Geographical Distributions

The ranges of TSP, IP and FP average concentrations in the western and eastern parts of the United States are presented in Table 6.2.1. The SURE ranges (except for the low end of TSP) are in agreement with those found by the IP Network, lending credence to the regional representativeness of the sites in both networks since the measurements were derived from different sites at different times.

The first feature of this regional comparison is that the ranges in the West for TSP and IP are larger than the ranges in the East and that western FP average concentrations are lower than eastern averages in that size range. Part of this is due to the selection of sites. Hawaii has little industry and little pollution transported to it, aside from marine aerosol, from outside. It must represent one of the

TABLE 6.1.4

SEASONAL AND ANNUAL ARITHMETIC AVERAGES OF TSP, IP, AND FP AT NINE SURE SITES

SURE Site ID	SURE Site	August, 1977 (ug/m³)	October, 1977 (ug/m³)	January, 1978 (ug/m³)	April, 1978 (ug/m³)	July, 1978 (ug/m³)	October, 1978 (ug/m³)	15 Month[b] Average (ug/m³)
01	Montague, MA	30/30/24[a]	18/18/14	15/18/15	17/16/11	33/36/27	21/21/14	22/23/17
02	Scranton, PA	91/40/26	40/21/13	29/20/14	43/22/12	87/43/27	57/26/15	58/29/18
03	Indian River, DE	41/40/23	29/23/16	31/26/19	37/29/19	35/35/22	37/29/16	35/29/19
04	Duncan Falls, OH	42/37/23	36/28/17	45/28/23	45/29/16	49/42/27	38/23/13	42/31/20
05	Rockport, IN	44/35/23	53/35/19	53/39/29	54/32/19	66/46/29	57/33/18	55/37/23
06	Giles County, TN	43/29/19	37/26/16	29/25/20	58/29/17	49/36/23	46/32/17	43/29/19
07	Ft. Wayne, IN	42/30/21	35/23/17	51/31/26	34/24/16	45/38/22	34/25/14	40/28/20
08	RTP, NC	41/29/20	30/22/17	26/24/18	39/27/17	40/34/25	38/30/22	36/28/20
09	Lewisburg, WV	32/25/17	26/16/11	29/21/17	28/22/14	33/30/21	30/20/13	30/22/16
	Average for all sites	45/33/22	34/24/16	34/26/20	39/26/16	49/38/25	40/27/16	40/28/19
	Maximum Average	91/40/26	53/35/19	53/39/29	58/29/19	87/46/29	57/33/22	58/29/23

[a] Format is TSP/IP/FP.

[b] Average of six seasonal averages.

TABLE 6.1.5

SEASONAL AND ANNUAL 24-HOUR MAXIMA OF TSP, IP, AND FP AT NINE SURE CLASS I SITES

SURE Site ID	SURE Site	August, 1977 (ug/m^3)	October, 1977 (ug/m^3)	January, 1978 (ug/m^3)	April, 1978 (ug/m^3)	July, 1978 (ug/m^3)	October, 1978 (ug/m^3)	15 Month Maximum[b] (ug/m^3)
01	Montague, MA	64/ 65/55[a]	50/47/38	31/ 62/56	38/34/23	82/ 92/68	44/61/41	82/ 92/68
02	Scranton, PA	217/102/68	78/46/27	97/ 56/39	131/50/24	215/101/81	165/51/33	217/102/81
03	Indian River, DE	70/ 72/34	56/45/44	56/ 59/49	73/58/45	84/ 90/63	92/61/28	92/ 90/63
04	Duncan Falls, OH	80/ 47/33	65/53/36	89/ 43/46	67/41/27	87/ 76/47	163/39/22	63/ 76/47
05	Rockport, IN	68/ 55/52	184/96/38	197/120/86	100/62/39	114/ 72/56	106/55/34	197/120/86
06	Giles County, TN	84/ 57/40	73/46/29	55/ 44/40	254/56/34	80/ 56/51	93/65/32	254/ 65/51
07	Ft. Wayne, IN	77/ 54/52	72/47/38	97/ 56/46	58/39/36	101/ 84/61	98/55/26	101/ 84/61
08	RTP, NC	76/ 55/43	49/41/33	43/ 36/31	98/57/40	63/ 58/44	66/69/50	99/ 69/50
09	Lewisburg, WV	48/ 42/49	55/40/33	47/ 37/31	56/33/25	54/ 47/53	66/43/29	66/ 47/53
	Maximum for all sites	217/102/68	184/96/44	197/120/86	254/62/40	215/101/81	165/69/50	154/120/81

[a] Format is TSP/IP/FP.

[b] Maximum found during six months of sampling.

Table 6.2.1

RANGES OF NON-URBAN ARITHMETIC AVERAGES
IN THE WESTERN AND EASTERN U.S.
INCLUSIVE SAMPLING PERIODS OF TABLES 6.1.1 and 6.1.4

	TSP Range ug/m^3	IP Range ug/m^3	FP Range ug/m^3
West (IP Network)	33 to 88	16 to 59	6 to 15
East (IP Network)	38 to 55	21 to 34	15 to 23
East (SURE Class I)	22 to 55	22 to 37	16 to 23

Table 6.2.2

RANGES OF NON-URBAN MAXIMUM 24-HOUR CONCENTRATIONS IN THE WESTERN AND EASTERN U.S.
INCLUSIVE SAMPLING PERIODS OF TABLES 6.1.2 and 6.1.5

	TSP Range ug/m^3	IP Range ug/m^3	FP Range ug/m^3
West (IP Network)	57 to 240	56 to 171	11 to 55
East (IP Network)	85 to 161	51 to 78	31 to 57
East (SURE Class I)	66 to 254	47 to 120	47 to 81

most pristine sites in the IP Network. Clint, Texas is subject to duststorms on occasion which will elevate the larger particle concentrations. The remaining western sites in Winemucca and Sauvie Island exhibit TSP and IP within the range of the eastern sites.

The generally lower average concentrations of FP in the West compared to the East are associated with lower densities of industrial emissions in the West and possibly with differences in synoptic-scale meteorology. A number of studies (compare Pierson, 1980; Heisler et al 1980, for example) have shown eastern aerosol to contain a greater proportion of sulfate than western aerosol while the western aerosol, as in the cases of Winemucca and Clint which are in arid, desert-like areas, tends to be enriched in geological material over the eastern aerosol. The sulfate is primarily in the FP fraction while the majority of the geological material is concentrated in the coarse fraction of IP and TSP.

The ranges of maximum concentrations are presented in Table 6.2.2. It is more difficult to compare maximum values than it is to compare averages because of the random nature of individual measurements taken at different times. The maximum TSP and IP concentrations in the West correspond to the Clint site and are consistent with the duststorm activity already mentioned while the Hawaii site shows the lowest values for TSP, IP and FP.

The differences from East to West are not so marked for the maxima as they are for the averages. None of the maximum TSP values at these non-urban sites exceeds the primary standard of 260 ug/m^3.

The maximum concentrations vary substantially from site to site for all particle size ranges. Given the extreme differences between the air masses affecting the sites in the West, this is understandable. The air masses affecting sites in the eastern United States are similar, however, and the range of maximum concentrations exhibited by the eastern sampling sites might be, in part, due to some local emissions or meteorological events which affected the particular site on the date the sample was taken.

It is better to examine the averages to get an idea of regional variability in the East. The picture of IP and FP average concentrations is fairly well represented by the average of all the eastern annual averages for both IP Network and SURE sites. The nominal IP eastern regional average is 29 ug/m^3 for the IP Network data and 28 ug/m^3 for the SURE data while the FP regional average is 19 ug/m^3 for both data sets. This consistency between both averages, taken at different times and different sites supports the generalization that average non-urban eastern concentrations are 30 ug/m^3 and 20 ug/m^3 for IP and FP, respectively.

6.3 Seasonal Distributions

There seems to be no general seasonal trend in average or maximum concentrations at western sites. A few anomalies show themselves in the seasonal data; at Winemucca and Sauvie Island the Fall, 1979, maximum TSP values are less than the corresponding IP maxima and the TSP average is less than the FP average, but this is probably due to non-simultaneous sampling for TSP and IP.

In the eastern United States there is a tendency toward lower concentrations in all size ranges in the fall and winter months than in the spring and summer months. SURE Montague and Scranton sites are the most illustrative of this phenomenon, but it is evident in the averages of most eastern sites. IP and FP from the eastern IP Network were 36 and 23 ug/m^3 respectively during Summer, 1980 but were 27 and 18 ug/m^3 during Winter, 1980. In the SURE Network, all site averages of IP and FP were 33 and 22 ug/m^3 in August, 1977 and 38 and 25 ug/m^3 during July, 1978. However, these values were only 26 and 20 ug/m^3, respectively, during January, 1978. Snowcover in many areas can suppress the coarse fraction of IP during winter while the high humidity and temperatures of summer will increase the likelihood of SO_2 conversion to sulfate in the eastern United States. These hypotheses need to be tested for IP and TSP concentrations by examining the chemical composition of selected samples.

Maximum concentrations in the East do not seem to follow a general seasonal pattern. Though the maxima for all particle sizes at Montague (SURE site) occurred during the summer months, the maximum concentrations for Rockport (SURE site) occurred in January, 1978. Once again, maximum concentrations seem to be randomly occurring with many causative factors.

6.4 Non-Urban Contributions to Urban Concentrations

The geographical distributions of non-urban TSP, IP and FP concentrations presented in this chapter can be compared with the urban concentrations of Chapter 5 to come up with a rough estimate of that fraction of the urban concentration which does not originate within the urban area. Ranges of annual averages for non-urban and urban sites in the East and West are grouped in Table 6.4.1.

In all cases the upper end of the urban range of averages is higher than the corresponding upper end of the non-urban range. In the West, the highest urban averages are approximately double the non-urban averages for TSP, IP and FP. In the East, they are nearly double for TSP and IP, but only half again as large for FP. A fair amount of the FP in eastern cities seems to be of a regional-scale rather than urban-scale nature.

The averages of concentration averages at urban and non-urban sites over the entire United States gives a rough cut of the nominal fraction of the urban aerosol which could be the result of transport into the urban area. This fraction must be considered an upper limit since even well-located regional-scale sampling sites will be affected by localized sources to some degree. Up to 50 to 60% of the average TSP, 70% of the average IP, and 60 to 80% of the average FP found in urban areas could be accounted for by transported material.

A comparison of urban and non-urban concentrations is more accurate when measurements at a non-urban sampling site close to an urban sampling site are compared. Such a comparison of average concentrations is made in Table 6.4.2 where an IP Network urban site has been paired with an IP or SURE Network non-urban site which should sample the same types of air masses as the urban sites, but without the local sources.

The ratios of non-urban/urban average concentrations have been tabulated to gain an idea of the possible distributions of the

TABLE 6.4.1

RANGES AND AVERAGES OF ARITHMETIC AVERAGE CONCENTRATIONS AT URBAN AND NON-URBAN SITES IN THE WESTERN AND EASTERN U. S.

	TSP (ug/m^3)		IP (ug/m^3)		FP (ug/m^3)	
	Range	Average	Range	Average	Range	Average
West						
Urban Sites (IP Network)[a]	39 to 161	80	25 to 92	44	13 to 37	21
Non-Urban Sites (IP Network)[a]	33 to 88	54	16 to 59	34	6 to 15	11
East						
Urban Sites (IP Network)[b]	49 to 125	80	30 to 68	48	14 to 33	25
Non-Urban Sites (IP Network)[b]	38 to 55	46	21 to 34	29	15 to 23	19
Non-Urban Sites (SURE Class I)	22 to 55	40	22 to 37	28	16 to 23	19
All Urban Sites (IP Network)	39 to 161	80	24 to 92	46	13 to 37	23
All Non-Urban Sites (IP Network)	33 to 88	50	16 to 59	32	6 to 23	15

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[a] Includes West Coast.

[b] Includes East, Northwest, Midwest, South, Southwest.

TABLE 6.4.2
RATIOS OF NON-URBAN TO NEARBY URBAN CONCENTRATIONS OF TSP, IP AND FP

	Ratio of Arithmetic Mean Non-Urban/Urban		
	TSP	IP	FP
Northeast			
MA			
Montague, MA/E. Boston	.35	.56	.77
" /E. Boston	.46	.68	.89
NY			
Big Sister, NY/P.S. No. 26	.35	.33	.52
" /P.S. No. 28	.33	.40	.64
" /Wilmuth	.25	.64	.72
Midwest			
OH			
Duncan Falls, OH/Akron	.59	.57	.66
" /Cincinatti	.76	.74	.77
" /Steubenville	.42	.49	.53
South			
AL			
Giles County, TN/S. Birmingham	.73	.62	.83
" /N. Birmingham	.52	.55	.86
" /Inglenook	.36	.48	.73
" /Mtn. Brook	1.08	.83	1.12
" /Tarrant City	.31	.33	.44
Southwest			
TX			
Clint, TX/El Paso	.79	.76	.42
West			
OR			
Sauvie Island, OR/Portland	.49	.43	.52
All Non-Urban/Urban Sites	.56	.65	.71

portions of the urban concentrations which could be attributable to non-urban aerosol. These ratios are crude estimates, since the urban and non-urban sites are not always close to each other (Figures 6.1.1 and 3.1.1 will locate the relative positions of sampling sites) and the measurements do not encompass the same periods of time. The averages of IP Network data were calculated from the data acquired over the periods listed in Table A.1 which went through the filtering of inequalities 3-1 to 3-4. SURE averages were taken from Table 6.1.4.

The range of ratios for TSP is the largest, as is to be expected since the largest particles, (greater than 15 um diameter), are rarely transported far and are likely to be of local origin. Up to 31% to 100% of the urban TSP concentrations could come from outside the urban area, though the mode seems to be in the 50 to 60% range.

For IP, 33 to 83% of the urban average concentrations can be found at nearby non-urban sites, though the majority of values are in the 55 to 75% range.

For FP, the non-urban/urban ratio of averages ranges from 42 to 100% with a large number in the 65 to 80% range.

The extreme cases can be explained in several ways, mostly by looking at the site surveys of Table 3.1.3. Mountain Brook, AL, for instance, is practically a non-urban site, being located on the outskirts of town, so it is expected to receive little local influence. Clint, Texas experiences the same duststorm activity as El Paso, but not the winter burning for heating that occurs in El Paso and Juarez, so the TSP and IP non-urban/urban ratios are high whereas the FP ratio is low.

These specific site comparisons, even in their crude form, support the generalization made from the grand mean ratios of non-urban/urban average concentrations: upper limits of 50% of the TSP, 60% of the IP and 70% of the FP are not subject to the control of emissions within the specific urban area being sampled, particularly in the eastern United States.

If an urban area is found in non-attainment of a new standard, practical control strategies may require regional in addition to local planning. The regional-scale monitoring data, aside from the now non-existent SURE Network and the few sites available in the IP Network, is presently inadequate to provide a technical basis for such planning.

Several generalizations can be made from the non-urban measurements and their comparison with urban measurements:

- Non-urban average TSP, IP and FP concentrations are nominally 50, 30 and 10 ug/m^3, respectively, in the western United States and 50, 30 and 20 ug/m^3, respectively, in the eastern United States. The number of non-urban sites with sufficient data in the West is small, however, and these observations should carry less weight than those from the East where independent measurements corroborate each other.

- There is a general seasonal variability of average TSP, IP and FP concentrations in the eastern United States in which the spring and summer month concentrations are elevated with respect to the fall and winter months. Independent measurements from different networks support this conclusion. Though the measurements in the western United States do not show a significant deviations between seasons, the number of sites examined is too saml1 to allow a general conclusion.

- Up to 50% of the TSP, 60% of the IP, and 70% of the FP in urban areas can typically be accounted for by concentrations present at nearby non-urban sites. This portion varies substantially from site to site and is based on a limited number of sites, primarily in the eastern United States. Much of the non-urban concentrations may have originated from far away anthropogenic sources.

CHAPTER 7

STATISTICS OF THE IP NETWORK CONCENTRATIONS

The primary air quality standards for suspended particulate matter are intended to protect public health with an adequate margin of safety. They are designed to prevent problems caused by long-term and short-term exposures to suspended particulate matter. Thus, the present particulate matter standard consists of two components; an annual component (75 ug/m^3 annual geometric mean) against which to judge long-term exposure and a 24-hr component (260 ug/m^3 not to be exceeded more than once per year) with respect to short-term exposure.

An area's attainment of these standards is determined by ambient sampling at representative sites according to a prescribed procedure and schedule. With regard to the present standard, 24-hr HIVOL sampling is required every sixth day at a location sufficiently removed from significant local sources of particulate matter (within approximately 200 feet).

Thus, two things determine whether or not an area is in attainment or non-attainment of the standard: the form of the standard with the values attached to it, and the measurement process used to obtain ambient concentrations to compare with those values. This section deals with the frequency of occurrence of different particulate matter concentrations and the statistics, particularly the mean and maximum value, derived from a finite set of samples.

First, the log-normal probability distribution is examined as a reasonable model for representing the population of particulate matter concentrations and for summarizing the large number of measurements taken in the IP Network. Next, the distributions of each size fraction at individual sites and over the whole network are examined. Finally, geometric and arithmetic means are compared as possible statistics for representing the true distributions and their variability as a function of sample size is studied. Because of the limited quantity of data available for examination, the cases studied are to be considered illustrative rather than conclusive. All data used in this chapter went through the screening procedure of inequalities 3-1 to 3-4.

7.1 The Log-Normal Frequency Distribution

Two issues must be addressed in the setting of an ambient air quality standard:

1. The determination of the actual long-term and short-term concentration levels.
2. The statistical form by which the exceedance of those levels is determined.

The second issue is important from a standard-setting (as opposed to a standard monitoring) point of view because any set of measurements taken to assess a sampling site's attainment of the standard is merely a statistical sample of all possible measurements. Even if 365 24-hr particulate matter samples per year are taken, this still represents a single random sample of size 365 from an infinite population of possible levels (Neustadter and Sidik, 1974). In most cases, the sample size will be less than 365 cases/year and estimates of the true mean and maximum concentrations must be made from this sample. These estimates are statistics which assume the cases are drawn from the same population. The precision with which these statistics are estimated decreases as the number of cases used to calculate them decreases. The estimate of the mean is not affected by the choice of an assumed statistical distribution of the population. The selection of a distribution can, however, change the estimate of a maximum value for a given number of days of sampling.

The log-normal distribution has long been used to represent the statistical population from which pollutant concentrations are drawn (Larsen, 1974, 1975, 1976). It offers some practical advantages over the more commonly known normal distribution in that:

- No negative values are allowed, which is consistent with ambient measurements.
- Histograms of the frequency of occurrence of various concentrations are skewed toward the lower concentrations.
- High concentrations receive lower weighting in the estimation of a geometric mean of a log-normal distribution than they do in the estimation of the arithmetic mean of a normal distribution.

No physical justification for a log-normal distribution of ambient pollutant concentrations has yet been found. Benarie (1971) first suggested that they are log-normally distributed because wind speeds are log-normally distributed. Making concentration predictions from a variety of dispersion models with log-normally distributed wind speeds as input, Bencala and Seinfeld (1976) concluded that "... if wind speeds are nearly log-normally distributed then resulting concentrations will be nearly log-normally distributed." They are careful to add the caveat that "this result does not establish that wind speeds are the primary influence on concentration distributions in the atmosphere, since other effects are most certainly influential."

Kahn (1973) showed that a log-normal distribution follows from the assumption that the change in pollutant concentration between successive measurements is proportional to the first measurement. He, too, admits that "the complexity of the emission-transport-receptor process makes it difficult, if not impossible, to prove that air pollutants are log-normal."

Studies of total suspended particulate matter (TSP) concentration distributions at a number of sites yield mixed results. Hovey et al (1976) and Phinney and Newman (1972) applied Kolmogorov-Smirnov and Chi-square goodness of fit tests to TSP data in New York and Indiana, respectively, and did not reject the hypothesis of log-normal distributions. Kalpasanov and Kurchatova (1976), however, did reject the log-normal hypothesis for TSP concentrations in Sofia, Bulgaria.

The most comprehensive studies of TSP concentration distributions were carried out by deNevers et al (1977, 1979). After examining 4,112 annual cumulative frequency distributions from HIVOL sampling sites in California, Georgia, Illinois, Missouri, New Hampshire, New York and Pennsylvania, they (deNevers et al, 1979) observed four patterns which occur in the mid-range of the data. Patterns 1, 2 and 3 are illustrated in Figures 7.1.1, a, b and c. Pattern 4 is the inverse of Pattern 3 with a horizontal section in the middle.

deNevers et al (1979) drew random samples of 25 and 75 values from a large set of random numbers generated from a log-normal

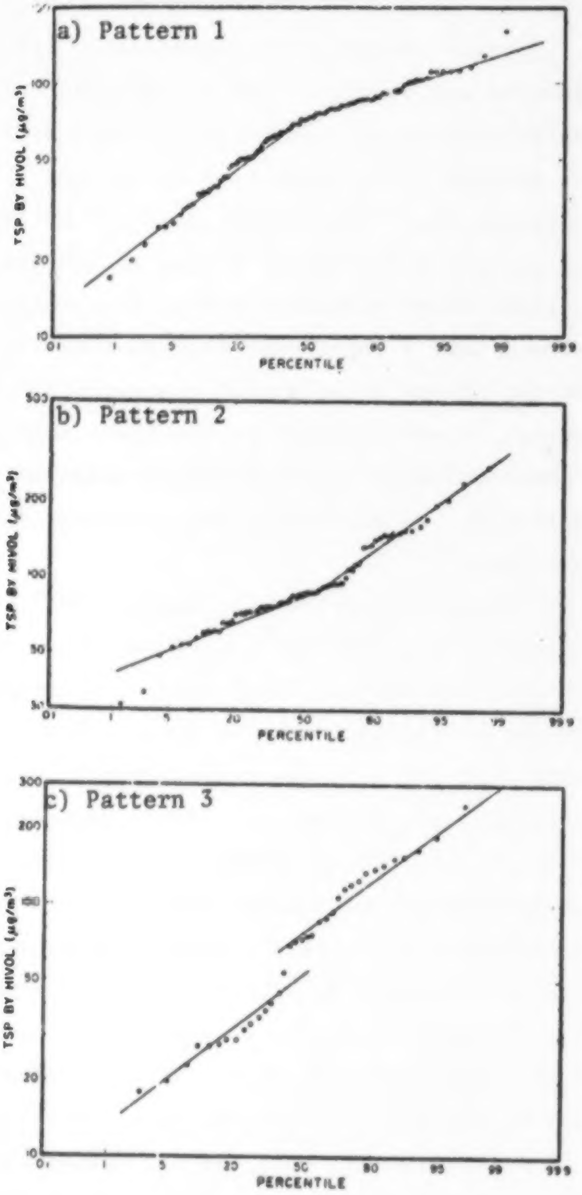

Figure 7.1.1 Patterns 1(a), 2(b), and 3(c) of TSP Frequency Distributions Found by deNevers et al (1979).

distribution and found excellent examples of Patterns 1, 2 and 3 (Pattern 4 did not frequently occur in the ambient or simulated data).

In agreement with other researchers, deNevers et al (1979) warn that each of the patterns in Figure 7.1.1 "....could have arisen by simple random sampling from truly log-normal populations of data. It is not convincing evidence that it did."

In search of this convincing evidence deNevers et al (1979) applied the Kolmogorov-Smirnov goodness of fit test to 3,992 of the annual distributions (patterns with extremely high or low end values were deleted from the original set as providing unrepresentative statistics and were eliminated from consideration). These tests yielded the result that most patterns appeared with frequencies similar to those to be expected if samples were drawn from random, log-normally distributed populations. The exceptions consisted of an inordinate number of Pattern 1. deNevers et al (1979) postulate that these cases might arise from samples being drawn from two independent log-normal distributions, each representing a distinctive meteorological regime.

Other distributions for suspended particulate matter concentrations have been proposed. Bencala and Seinfeld (1976) tested the three-parameter log-normal, the Weibull, and the Gamma distributions. Mage and Ott (1978) advocate a censored three-parameter log-normal model as a possible alternative to the traditional two-parameter log-normal distribution. deNevers et al (1979) propose the use of more than one log-normal distribution to represent one year of measurements (Mage, 1979).

It seems that the assumption of a log-normal distribution for suspended particulate matter concentrations is not completely supported by a physical rationale nor always by statistical measurements of validity. It is "....defensible on the grounds that it works" (Lodge and West, 1969), and that is considered sufficient justification for choosing it over others in order to present and evaluate size-classified suspended particulate matter concentrations collected in the IP Network.

The statistics of the extreme values of a distribution are not necessarily the same as the central part of the distributions, and nearly all log-normal plots of suspended particulate matter concentrations show deviations at the upper and lower concentration extremes (deNevers et al, 1977). Roberts (1979a) shows that when dealing with a "not to be exceeded..." type of standard applied to individual measurements, "the probability of exceedances.... is independent of the distribution of the random variable..." Roberts (1979b) shows several examples of this applied to gas concentration measurements.

The frequency distributions of TOTAL and FINE particulate matter measurements need to be studied to determine whether or not log-normal distributions and their associated statistics adequately describe the actual measurements for practical purposes even though fits to such distributions may not always be statistically significant.

7.2 Cumulative Frequency Distributions in the IP Network

Cumulative frequency distributions for all validated data specified in Table A.1 of Appendix A for all sites in the IP Network appear in Figure 7.2.1 a-e and are not necessarily representative of distributions at a single site. Each plot contains the calculated geometric average concentration and geometric standard deviation. In all cases these calculated values at the average, the average minus one standard deviation, and the average plus one standard deviation match fairly closely with the values read from each of the frequency distributions at the 50th, 16th and 84th percentiles, respectively. The central portion of each of these curves tends to approximate a log-normal distributions fairly accurately. It is obvious, however, that at the extremes there are substantial deviations from this distribution, particularly in the case of the TOTAL, FINE and COARSE suspended particulate matter concentrations. Approximately 3% of the FINE samples have concentrations less than 4 ug/m^3. Nearly 10% of the COARSE measurements are less than 5 ug/m^3, while 2% are less than 1 ug/m3. These extreme values propagate to the TOTAL distribution.

The central and upper extremes of the FINE and COARSE distributions are similar to each other, which is reasonable when one compares individual FINE/COARSE pairs and the average of FINE/COARSE ratios of 1.21. At the lower extreme, however, there exists a

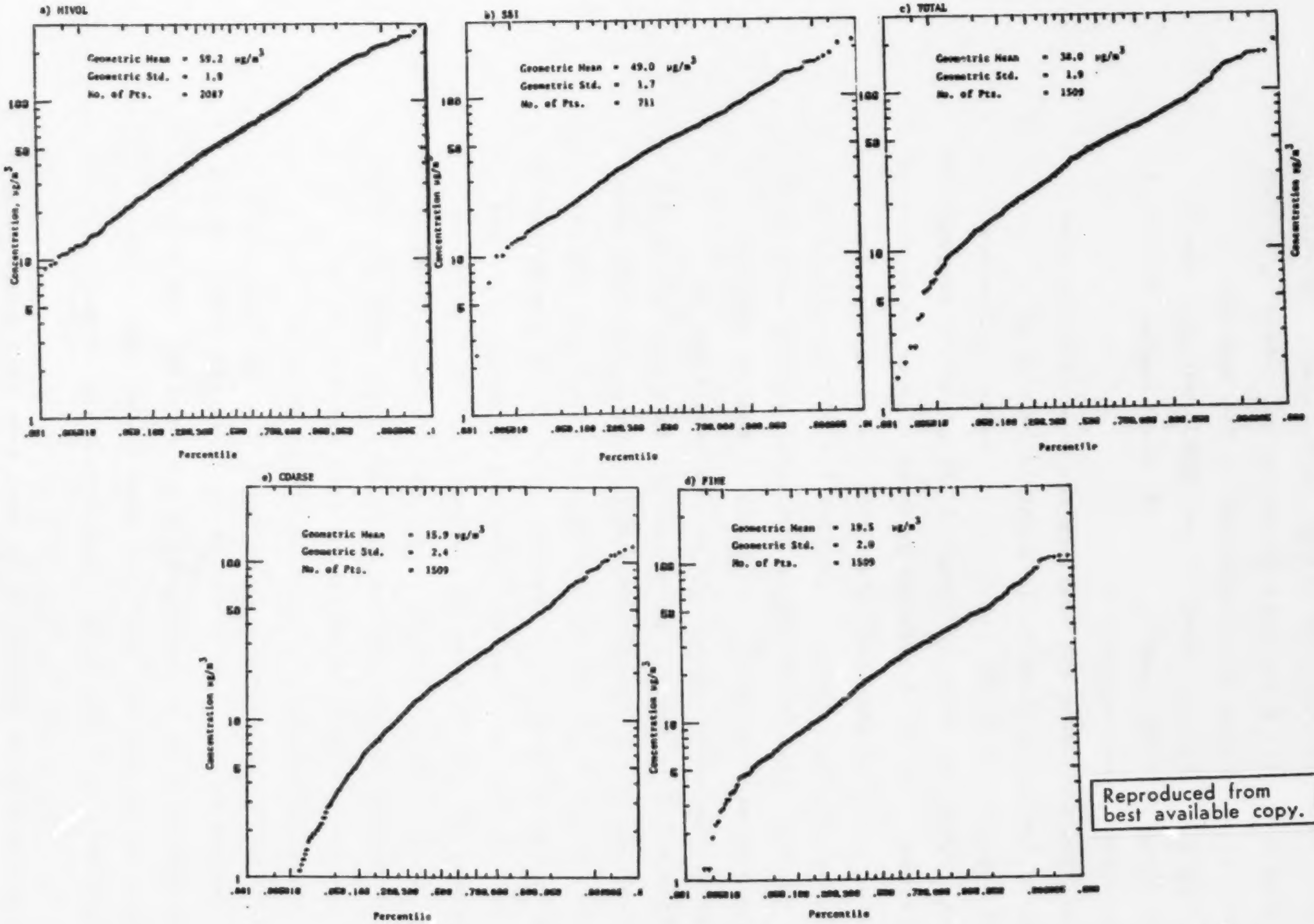

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Figure 7.2.1a-e - Cumulative Frequency Distributions of HIVOL(a), SSI(b), TOTAL(c), FINE(d), and COARSE(e) Concentrations for all Measurements in the IP Network. These Measurements are from 96 Sampling Sites.

disproportionate share of low COARSE concentrations, notwithstanding the elimination of many of these records according to the validation criteria of Section 3.4. As deNevers et al (1977) observed for HIVOL measurements, "...some of these low values, particularly the extremely low ones, are an artifact of the data gathering and recording system and most likely are not true representations of the atmospheric conditions." As noted earlier, some of the COARSE material may not adhere to the filter thereby causing many of those samples to exhibit lower than expected concentrations.

If the SSI and the TOTAL are sampling the same aerosol, then their cumulative frequency distributions should be similar. Comparison of Figures 7.2.1b and 7.2.1c show a marked difference between the distributions, both in terms of the geometric averages and the maximum values. The SSI distribution shows a lower proportion of values less than 10 ug/m^3 than does the TOTAL distribution. The proportion of high concentrations is greater for SSI than it is for TOTAL; 7% of the SSI measurement exceed 100 ug/m^3 whereas only 3% of the TOTAL values exceed 100 ug/m^3. Only 285 of the 771 SSI and 1,509 TOTAL were taken at the same site at the same time, so Figures 7.2.1b and 7.2.1c may not represent the same population. In fact, the proportion of SSI samples obtained in industrialized areas was considerably higher than the proportion of dichotomous samples taken in such areas. However, the preponderance of low concentrations shown by the FINE and COARSE distributions casts some doubt on the representativeness of some of these measurements.

As stated in Section 7.1, there is no reason to expect the distribution of ambient concentrations at a particular site to follow a log-normal curve, let alone measurements from various sites scattered all over the country. The value of the plots in Figures 7.2.1a-e is in conveniently summarizing all the data in the network in a concise manner. It is remarkable that the HIVOL and SSI concentrations appear to be so log-normally distributed, though given the large number of degrees of freedom, a statistical test might reject the hypothesis that they were drawn from a log-normal distribution.

The 99th percentile concentration as read from each graph gives a good indication of what the highest 1% of the concentrations in the network are, approximately 210 ug/m^3 for HIVOL, 170 ug/m^3 for SSI, 150 ug/m^3 for TOTAL, 80 ug/m^3 for FINE and 90 ug/m^3 for COARSE. The IP Network data presented in Figures 7.2.1a-e are highly dominated by measurements taken in the Philadelphia area (39% of the HIVOL, 59% of the SSI, and 29% of the TOTAL, FINE and COARSE values in the plots are from Philadelphia sites). Cumulative frequency distributions for all sites outside of Philadelphia were generated which yielded very nearly the same results as those in Figures 7.2.1a-e. SSI, TOTAL and FINE plots for data grouped by different site type classifications were similar, though they were often shifted upward or downward because the average concentrations for different site types were different. When the number of points dropped to less than 30, the linear part of the log-normal distribution disappeared in these plots.

For all sites where SSI or TOTAL measurements were 20 or greater, the SSI, TOTAL and FINE cumulative frequency distributions were plotted in an effort to see whether or not deNevers et al (1979) TSP patterns occurred for IP and FP measurements. Most sample sets contained fewer than 30 values, and the plots, in general, did not appear to follow any pattern. The best examples of deNevers et al (1979) from these plots are presented in Figures 7.2.2a-d. These may be compared with Figures 7.1.1a-c. It seems that the same types of patterns observed for TSP concentrations may be present in IP concentrations, but given the small number of measurements available from most IP Network sites at this time, it is too soon to tell. When more data become available, it would be useful to determine whether or not deNevers et al (1979) patterns exist and to test their hypothesis that they result from two different log-normal distributions related to different meteorological regimes. If TSP, IP and FP distributions from the same site and simultaneous samples exhibit the same patterns, it would reinforce the hypothesis that some environmental (as opposed to measurement) factor is causing the variability of the concentrations.

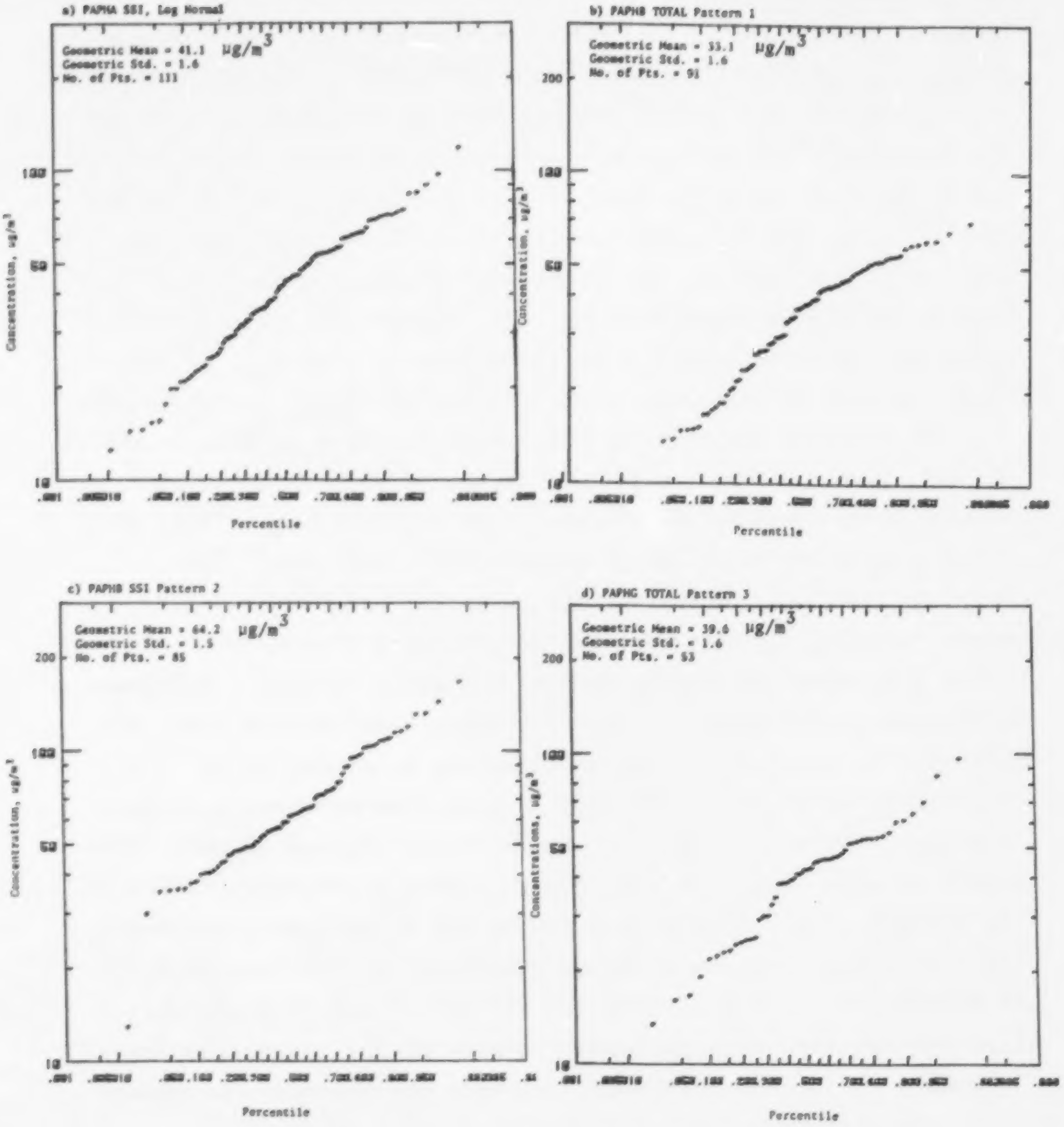


Figure 7.2.2 a-d Examples of Cumulative Frequency Distributions from Individual IP Network Sites Representing a Log-Normal (a), deNevers et al (1979) Pattern 1 (b), Pattern 2 (c) and Pattern 3 (d)

7.3 Arithmetic and Geometric Averages

Though a geometric average and standard deviation can be calculated from a set of ambient concentrations at a site and these parameters can describe a log-normal distribution which is close to, though not exactly equal to, the central part of the ambient measurement distribution, there are good reasons to formulate a long-term standard in terms of an arithmetic rather than a geometric mean (Mage, 1980):

- The arithmetic mean has physical significance for human health whereas the geometric mean does not. The integral of an ambient concentration times a breathing rate over time is proportional to an arithmetic rather than a geometric mean.
- The use of the arithmetic mean for the particulate matter standard will allow comparison with other average air quality data (such as SO_2) and provide more meaningful confidence intervals (an arithmetic mean has a symmetric confidence interval while that of a geometric mean is asymmetric).

In practice, the difference between the geometric average and the arithmetic average of a set of ambient suspended particulate matter measurements may be small enough to allow one to be estimated from the other. Mage (1980) calculated the arithmetic averages of the data used to support the present National Ambient Air Quality Standard for TSP and compared them with the geometric averages of the same data sets. The average ratio of the geometric to arithmetic average was .87 with a standard deviation of .02 for 21 pairs of averages. The ratios ranged from .82 to .92. Frank (1980) calculated and compared the geometric and arithmetic averages of TSP for 11,451 site-years included in the National Aerometric Data Base (NADB). He stratified these averages into four geometric average concentration ranges to identify variations with concentration. In the range which included the level of the TSP standard, the 61 to 90 ug/m^3 range, he found that out of 3,756 site-years, over 50% of the geometric/arithmetic average pairs differed by less than 11% and over 90% of the pairs differed by less than 20% from each other (it should be noted, however, that 1% of the pairs differed from each other by more than

44%). If the difference between averages for IP and FP is just as constant, then, depending on the precision required, little is lost in transferring from a geometric mean, which might be more descriptive of the distribution, to an arithmetic mean, which may be more closely related to health effects (Mage, 1980).

Arithmetic and geometric averages were calculated for all IP Network sites with available HIVOL, SSI, TOTAL and FINE measurements using data validated by inequalities 3-1 to 3-4 and the ratios of geometric to arithmetic averages were produced. The averages, ranges and standard deviations of these ratios for each sample type are presented in Table 7.3.1. The average for each size fraction is in the vicinity of .9 with standard deviations of approximately .05. This ratio varies with the scatter in the data. Sample sets having larger standard deviations (geometric or arithmetic) have lower and more variable ratios. Table 7.3.2 presents the distribution of ratios as a function of geometric standard deviation. As the geometric standard deviation increases, the ratio decreases. The range for a given standard deviation depends more on the number of samples than on the standard deviation. Most geometric standard deviations are in the neighborhood of 1.5 to 1.7 for all size fractions. In this neighborhood, the ratio varies from .85 to .95 for all samples.

As long as both averages can be calculated from a set of data, it makes no difference which average is chosen. The calculated average is only an estimate of the true mean, however, and its precision depends on the sample size. The calculation formulas for the geometric and arithmetic averages are derived from maximum likelihood theory (Meyer, 1978) to provide the most probable estimate of the mean based on a log-normal or normal distribution, respectively. Different sample sizes will give different estimates of the true mean, and if the assumed distribution (log-normal or normal) is closer to the real distribution of particulate matter concentrations, the calculated average (geometric or arithmetic) from a given number of samples will be closer to the true mean.

This is studied from a practical standpoint in Table 7.3.3 where the ratios of geometric to arithmetic averages are calculated for data sets which assume 3, 6, 12, 24 and 48 days between samples. The data

TABLE 7.3.1

AVERAGE RATIOS OF GEOMETRIC TO ARITHMETIC AVERAGES AT IP SAMPLING SITES

Sample Type	Number of Averages	Average Ratio Geometric Average/ Arithmetic Average	Standard Deviation of Ratio	Range of Ratio
HIVOL	82	.91	.05	.70 to .98
SSI	37[a]	.91	.07	.63 to .98
TOTAL	70	.90	.05	.71 to 1.00
FINE	70	.88	.06	.69 to .98

[a] Site OHMEA eliminated as outlier.

TABLE 7.3.2

AVERAGE RATIOS AS A FUNCTION OF GEOMETRIC STANDARD DEVIATION FOR IP SAMPLING SITES

Sample	Geometric Standard Deviation ug/m^3	Range of Ratio of Geometric Average to Arithmetic Average	No. of Ratios	Range of Number of Data Pairs in Each Ratio
HIVOL	1.2	.98 to .99	4	3 to 9
	1.3	.96 to .98	7	3 to 16
	1.4	.94 to .95	9	14 to 38
	1.5	.91 to .95	15	5 to 48
	1.6	.88 to .92	19	6 to 107
	1.7	.87 to .94	19	2 to 99
	1.8	.87 to .87	2	35 to 41
	1.9	.81 to .85	3	6 to 26
	2.1	.78 to .78	1	27 to 27
	2.6	.70 to .70	1	12 to 12
SSI	1.2	.98 to .99	3	2 to 5
	1.3	.97 to .98	3	2 to 12
	1.4	.94 to .97	7	7 to 25
	1.5	.91 to .95	6	2 to 85
	1.6	.89 to .94	9	2 to 111
	1.7	.87 to .90	4	7 to 35
	1.8	.85 to .86	2	9 to 33
	2.0	.79 to .81	2	10 to 14
	3.6	.63 to .63	1	6 to 6

TABLE 7.3.2 (Continued)

Sample	Geometric Standard Deviation ug/m^3	Range of Ratio of Geometric Average to Arithmetic Average	No. of Ratios	Range of Number of Data Pairs in Each Ratio
TOTAL	1.1	1.0 to 1.0	1	2 to 2
	1.2	.98 to .98	1	3 to 3
	1.3	.96 to .97	3	9 to 22
	1.4	.94 to .98	6	2 to 35
	1.5	.91 to .94	19	4 to 49
	1.6	.88 to .92	19	7 to 91
	1.7	.86 to .89	4	13 to 25
	1.8	.85 to .88	7	3 to 33
	1.9	.82 to .88	4	5 to 29
	2.0	.81 to .85	3	10 to 35
	2.2	.77 to .78	2	9 to 19
	2.7	.71 to .71	1	9 to 9
FINE	1.3	.97 to .98	2	2 to 9
	1.4	.94 to .96	4	3 to 35
	1.5	.90 to .94	7	9 to 43
	1.6	.88 to .94	20	2 to 51
	1.7	.85 to .90	15	13 to 91
	1.8	.83 to .86	4	28 to 49
	1.9	.82 to .87	8	9 to 25
	2.0	.77 to .85	4	5 to 29
	2.1	.78 to .85	3	3 to 14
	2.3	.69 to .72	2	26 to 35
	3.0	.69 to .69	1	19 to 19

TABLE 7.3.3

VARIABILITY OF THE RATIOS OF GEOMETRIC AND ARITHMETIC AVERAGES WITH SAMPLING FREQUENCY

Sampling Site	Sampling Intervals (days)					
	3	6	12	24	48	Range of Sample Size
	Ratio of Geometric to Arithmetic Average					
500 S. Broad (PAPHA)						
HIVOL	.92	.94	.95	.95	.94	113 to 7
SSI	.90	.91	.92	.91	.88	111 to 8
TOTAL	.93	.94	.99	.99	.99	43 to 4
FINE	.92	.92	.96	.98	.99	43 to 4
Allegheny (PAPHB)						
HIVOL	.87	.88	.89	.91	.98	99 to 7
SSI	.91	.92	.93	.94	.97	85 to 5
TOTAL	.92	.95	.96	.97	.96	20 to 2
FINE	.90	.96	.97	.97	.96	20 to 2
NE Airport (PAPHE)						
HIVOL	.91	.90	.92	.96	.95	82 to 7
SSI	.94	1.00	-	-	-	2 to 1
TOTAL	.91	.90	.93	.95	.95	91 to 6
FINE	.89	.87	.91	.92	.88	91 to 6
Presbyterian Home (PAPHG)						
HIVOL	.91	.94	.95	.94	.96	98 to 7
SSI	.95	1.00	-	-	-	2 to 1
TOTAL	.90	.94	.93	.96	.94	53 to 4
FINE	.88	.93	.92	.95	.91	53 to 4
St. John's (PAPHI)						
HIVOL	.91	.90	.88	.92	.91	107 to 8
SSI	.89	.90	.88	.92	.89	96 to 6
TOTAL	.88	.88	.85	.99	-	18 to 3
FINE	.88	.86	.84	1.00	-	18 to 3

set is essentially halved from one interval to the next and the number of samples used to calculate the averages for the 3-day and 48-day intervals is listed in the last column.

The ratios of the geometric average to the arithmetic average rarely vary by more than .03, even when the initial sample size is reduced by a factor of 16. When significant changes do occur, the total number of samples is normally less than ten.

These case-studies indicate that both the geometric and arithmetic averages are of equal value in representing the distribution of ambient concentrations for all particle size ranges and reasonable numbers of measurements. If an arithmetic mean is deemed more representative of exposure levels, then a standard which is specified in terms of such a mean seems reasonable. These studies are not as extensive as those of Frank (1980), however, who did find large differences between geometric and arithmetic averages for data from a small number of site-years. More comparisons of these averages of SSI, TOTAL and FINE measurements should be made.

7.4 Variability of Means and Maxima with Sample Size

Every statistic is an estimate calculated from a finite sample drawn from a larger (often infinite) population. The frequency of sampling and the total number of samples available will affect the estimates of the mean and maximum values for particulate matter concentrations in all particle size ranges. Akland (1972) describes a practical method of assessing the adequacy of a sample size. He used 6 years of TSP measurements which resulted from daily measurements in Buffalo, NY. He calculated the annual arithmetic average TSP concentrations for each of these years using all samples, the samples on every third day, and the samples on every 13th day. The maximum deviation from the population mean was +.9% for the third day subset and -8.0% for the 13th day subset. The standard deviations of the subsets and the population were nearly the same.

Five sites in the IP Network collected enough data (approximately every third day for one year) to make such a comparison possible for the size-classified concentrations. While five sites are not sufficient to form sweeping generalizations, they are sufficient to illustrate the types of effects different sampling frequencies can have on the statistics calculated from their measurements. The data records for the 500 S. Broad, Allegheny, NE Airport, Presbyterian Home and St. John's sampling sites in Philadelphia were successively halved by removing every other data record. This is equivalent to, though not exactly the same as, sampling every 3rd, 6th, 12th, 24th and 48th day. It is not exactly the same because sometimes samples were taken more often than every third day, and in some cases no sample was taken on a particular day. This procedure is legitimate because it simulates what would happen under normal sampling conditions. In a routine sampling program, some extra samples are taken and others are lost. Table 7.4.1 shows that this procedure generally halved the number of samples from one sampling interval to the next except when the number of records became very small, i.e. less than five. The arithmetic averages of each of these subsets were calculated for each size-classified sample and the results are plotted in Figures 7.4.1a-d.

The important feature to note in these figures is the variability of the averages as the interval between samples increases and as the number of samples used to calculate the average decreases. The cases considered in Figures 7.4.1a-d do not show general upward or downward trends in average concentrations with sample size; these trends cannot be expected because of the random way in which samples used to calculate each average were selected. The average calculated from the rejected data set after each split would provide an equally valid estimate of the true mean. If an average shown in one of the plots of Figures 7.4.1a-d for a given sampling interval is a certain amount less than the previous average resulting from more frequent sampling, the average calculated from the rejected data set is greater than the previous average by the same amount. For clarity, only the averages from the data sets corresponding to the pre-ordained sampling schedule are shown.

Some of the arithmetic averages vary substantially as a function of sample size. SSI at Presbyterian Home and NE Airport can be dismissed as having too small a sample size. St. John's FINE and TOTAL averages show extreme variations by the time the original

TABLE 7.4.1

NUMBER OF MEASUREMENTS IN SUBSETS OF ALL MEASUREMENTS AT PHILADELPHIA SITES

Sampling Site & Size Fraction	Days Between Samples 3	6	12	24	48
500 S. Broad (PAPHA)	No. of Measurements				
HIVOL	113	50	29	15	7
SSI	111	57	28	15	8
TOTAL	43	21	11	5	4
FINE	43	21	11	5	4
Allegheny (PAPHB)	No. of Measurements				
HIVOL	99	49	27	14	7
SSI	85	44	23	11	5
TOTAL	20	10	5	3	2
FINE	20	10	5	3	2
NE Airport (PAPHE)	No. of Measurements				
HIVOL	82	41	21	12	7
SSI	2	1	-	-	-
TOTAL	91	48	24	12	6
FINE	91	48	24	12	6
Presbyterian Home (PAPHG)	No. of Measurements				
HIVOL	98	48	23	13	7
SSI	2	1	-	-	-
TOTAL	53	25	14	8	4
FINE	53	25	14	8	4
St. John's (PAPHI)	No. of Measurements				
HIVOL	107	54	28	14	8
SSI	96	50	24	12	6
TOTAL	18	10	5	3	-
FINE	18	10	5	3	-

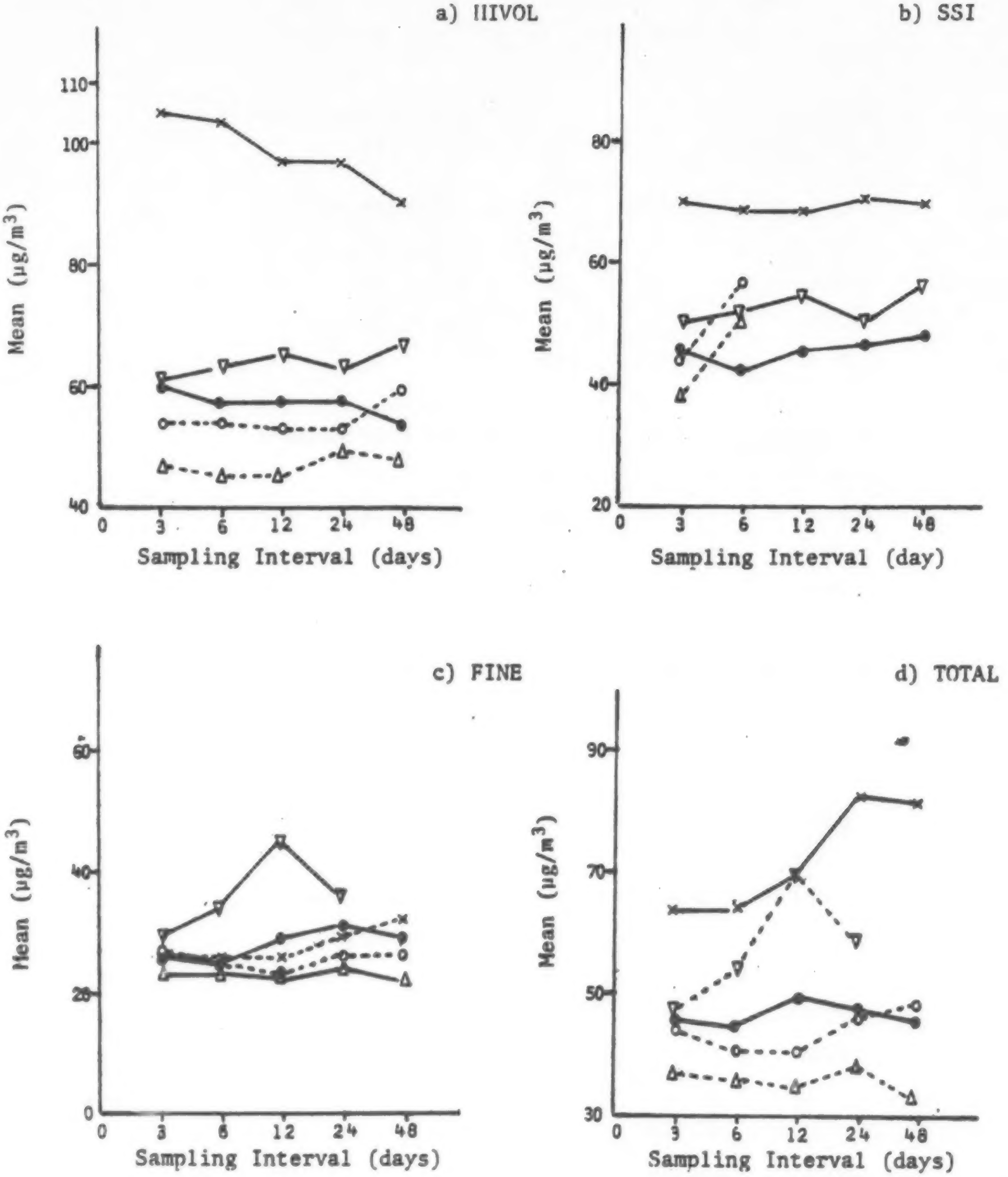


Figure 7.4.1 a-d Arithmetic Average Concentrations for Different Sampling Intervals at 500 S. Broad(●), Allegheny(x), NE Airport(Δ), Presbyterian Home(o), and St. John's(∇) for HIVOL(a), SSI(b), FINE(c), and TOTAL(d).

18 values captured with the 3-day interval (values weren't available every third day, but the situation is analogous to what would happen if many randomly occurring samples were invalidated, a very real field problem) are reduced to 5 values with the 12-day intervals; TOTAL averages at Allegheny begin with 20 samples for the 3-day interval, end with 2 samples for the 48-day interval and show the same deviations. FINE averages at Allegheny, however, do not vary by more than 5% until the number of samples is reduced to three for the 24-day sampling interval.

In general, when the number of samples used to calculate the average falls below 15, there is often, though not always, an abrupt change in the average concentration estimate. In most cases, this corresponds to the 24 or 48-day sampling interval.

Except for the case of Allegheny, the variability of the averages with sample size (or sampling interval) is essentially equivalent for all site types (as Table A.1 of Appendix A shows, these five sites represent a number of different site classifications) and for all particle sizes sampled in the IP Network until the number of samples in the average is approximately 15 or less. The averages of the less frequent sampling schedules (sampling interval of 12-day instead of 3-day) are within ±10% of the averages calculated from the 3-day schedule for most cases. The same conclusion would also be drawn if all the subsets were individually examined.

The case of Allegheny is interesting in that both HIVOL and SSI averages contain a large number of samples (113 and 99, respectively, for the 3-day intervals) but the HIVOL averages show considerable variability as the sampling interval is increased whereas the SSI averages remain nearly constant. Allegheny (see Table 3.1.3) is a site which is influenced by a number of nearby non-ducted area sources; many of the individual HIVOL measurements are high and vary from day to day. The SSI concentrations are not as variable. It appears that for this type of site, an average concentration estimate for a size-classified sample requires fewer individual measurements than does an average for TSP. In certain situations, the temporal concentration homogeneity introduced by the removal of highly variable, local source contributions of particles with diameters greater than 15 um might offer the advantage of reducing the number of samples required to estimate the true mean.

The maximum concentrations from each one of these data sets are shown for the five sites and particle sizes in Figures 7.4.2a-d. Estimates of the true maximum concentration are severly dependent on the sampling interval for all particle sizes. An important point in all the plots is that the maximum concentration always goes down as the sampling interval increases. The decrease in the maximum concentration is not a function of sampling interval. Sometimes a maximum value will persist through all cuts of the data set, as for the HIVOL maximum at Presbyterian Home. At St. John's the maximum value persists for three cuts for all sizes. The maximum drops sharply and remains the same for the remaining cuts for 500 S. Broad SSI and Allegheny FINE and COARSE. As the plots show, the decrease in maximum concentration from one set to the next can be quite large for all site classifications and particle sizes. The greatest decrease is for Allegheny HIVOL which falls by over a factor of two between the 6-day and 12-day sampling intervals. Even for the change between the 3-day and 6-day periods, the maximum decreases by over 35% for all particle size fractions at 500 S. Broad and for FINE and TOTAL at Allegheny and Presbyterian Home. In contrast to the average concentrations, which generally do not change substantially when sampling intervals are lengthened, the maximum concentration is very sensitive to the number and frequency of samples.

If a new standard is couched in the same terms as the present standard, an annual average and a 24-hr maximum (or 2nd maximum), then sampling intervals of up to 12 days seem adequate to assess the average, but not the maximum. Under such a standard, the best strategy of a region desiring compliance with a 24-hr standard would be to perform the minimum amount of sampling allowed. As Figure 7.4.2a shows, the samplers at 500 S. Broad, Allegheny and NE Airport may be penalizing themselves by sampling every third day instead of every sixth day as required by the reference method for TSP compliance monitoring. The same holds true for IP (both TOTAL and SSI measurements) and FP concentrations. This means that the monitoring

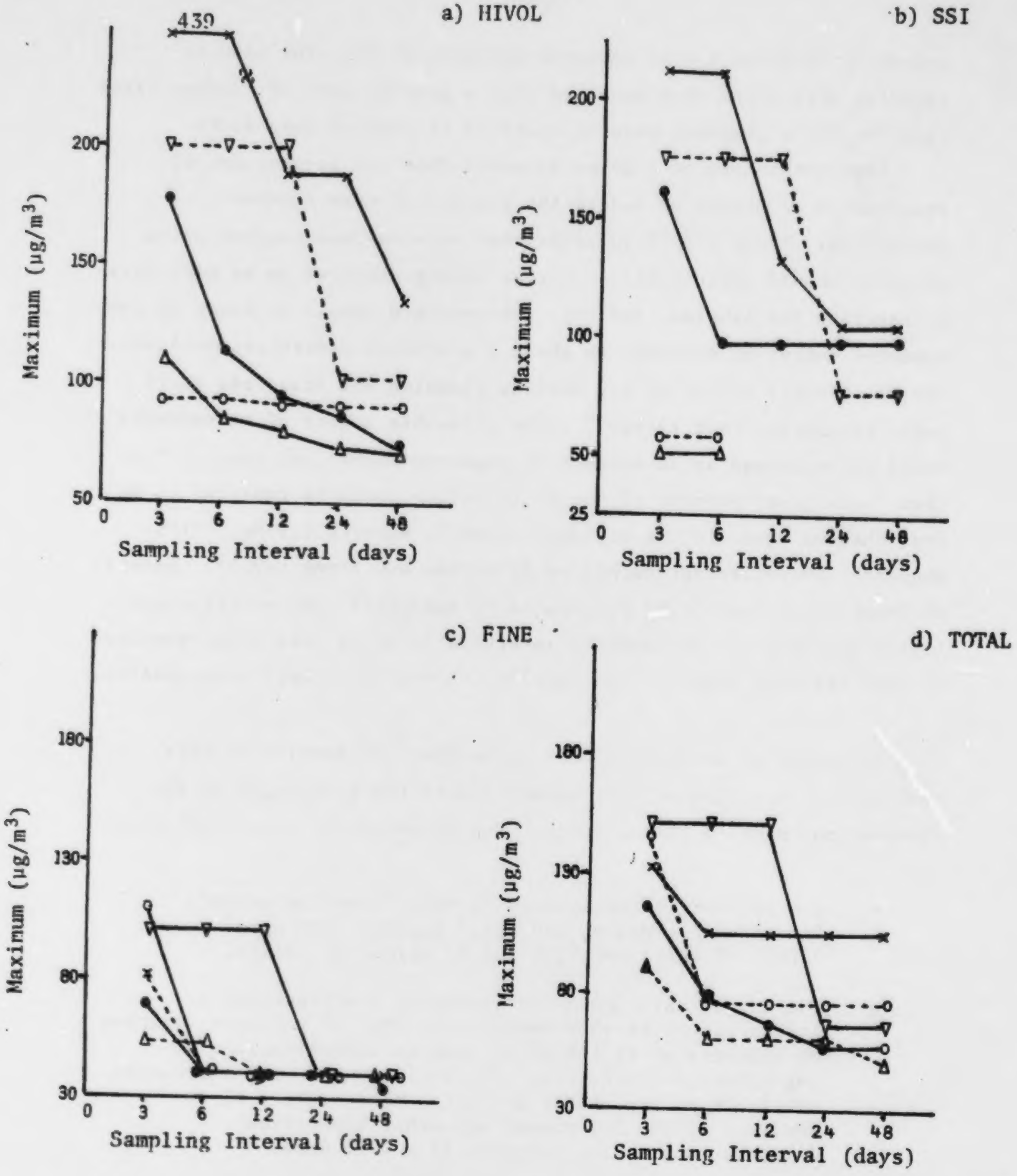


Figure 7.4.2 a-d Maximum Concentrations for Different Sampling Intervals at 500 S. Broad(●), Allegheny(x), NE Airport(Δ), Presbyterian Home(o), and St. John's(∇) for HIVOL(a), SSI(b), FINE(c), and TOTAL(d).

agency which gains a more accurate estimate of the true mean by sampling more often than required runs a greater risk of noncompliance with the 24-hr standard than it would if it sampled less often.

Some other form of a 24-hr standard than the present one is required to eliminate or reduce the penalty of more frequent monitoring. Frank (1981) suggests that each maximum concentration measured should additionally count as having occurred on as many days as separate the samples, and that the standard should be based on the expected number of exceedances above a specified concentration level. The EPA (1981b) Office of Air Quality Planning and Standards Staff paper recommends that either "...the allowable number of exceedances would be expressed as an average or expected number per year...," or that "...a given percent of the daily values would be expected to be less than or equal to the standard level." Roberts (1979a, 1979b) suggests some other approaches as do Curran and Frank (1975). Several of these forms need to be formulated by qualified statisticians and tested by changing the sampling intervals of large data sets, similar to what has been done in this section, to evaluate their practicality.

It should be emphasized once again that the paucity of data available at the time of this report limits the generality of the observations made in this chapter. The illustrative cases indicate:

- One percent of the IP Network measurements exceeded 210 ug/m^3 for HIVOL, 170 ug/m^3 for SSI, 150 ug/m^3 for TOTAL, 80 ug/m^3 for FINE and 90 ug/m^3 for COARSE.

- The log-normal cumulative frequency distributions at individual sites show examples of the TSP patterns advanced by deNevers et al (1979) as well as approximations to log-normal distribution. The small number of measurements available at most sites prevents an assessment of the adequacy of the log-normal and other statistical distributions in representing IP and FP data.

- The geometric averages of IP and FP data sets normally differ by 5 to 15% from the corresponding arithmetic averages, though the difference is as large as 37% for IP

Network data. The ratios of geometric to arithmetic averages calculated from subsets of all possible measurements containing decreasing numbers of measurements at a site are constant to within ±5% until the number of measurements in the subset falls below five.

- Arithmetic averages of IP and FP tend to remain constant, within ±10%, as the interval between samples is doubled and the number of samples is decreased. For 15 or fewer samples this consistency breaks down.
- Maximum concentrations of IP and FP are extremely sensitive to sample size and can be reduced by 50% as the interval between samples is increased. This means that any standard, such as the present one, which specifies a maximum concentration should also specify a sampling frequency or that other forms of short-term standards should be considered.

CHAPTER 8

PREDICTING IP CONCENTRATIONS FROM TSP CONCENTRATIONS

Given numerical values associated with a 24-hr maximum and yearly mean for a size-classified standard, communities must make some assessment of the extent to which they attain those values. Ultimately, this task can only be accomplished via actual ambient monitoring using samplers and procedures which meet the particle size collection specifications of the standard. The deployment of a new sampling network will not take place immediately, however, and in the interim, estimates of size-classified aerosol concentrations must be made for planning and network design purposes.

Many HIVOL TSP measurements exist at a wide variety of sites throughout the United States. In Chapter 2 it was demonstrated that, for a given size distribution and wind speed, relationships between IP and TSP measurements can be established; these derived relationships agreed remarkably well with the averages of many measurements. It is tempting to use these relationships to estimate IP and FP concentrations from TSP concentrations. A substantial uncertainty is associated with this estimate, however, and it is important to evaluate the magnitude of that uncertainty.

In this chapter, the validity of a receptor-oriented model for estimating IP from TSP concentrations is formulated and evaluated. This process involves:

- Deriving average slope and linear regression relationships between IP, FP and TSP measurements using IP Network measurements.
- Calculating the parameters of these relationship for data sets stratified by site type and HIVOL concentration range to evaluate whether or not such stratification improves the predictive ability of the model.
- Evaluating the accuracy of a model derived at one site over a period of time to predict IP concentrations at another site for the same time period.

- Evaluating the accuracy of a model derived at a site over a given period of time to predict IP concentrations at the same site over a different time period.

Once again, the caveat concerning the illustrative rather than conclusive nature of this treatment needs to be emphasized; IP Network data from which these models are derived are still limited. The methodology followed here may be useful for specific applications, but the actual models used in a given situation should be tested with more exhaustive sets of data to verify their predictive abilities. All measurements used in this chapter were screened by inequalities 3-1 to 3-4.

8.1 A Receptor Model Approach

Two approaches to estimating IP and FP concentrations are available, one source-oriented and the other receptor-oriented.

In the source-oriented approach an inventory of particulate matter emission rates in the appropriate size range is formed using emission factors (Shannon et al, 1980) and size-classified source sampling (Harris and Smith, 1980). With appropriate meteorological input, the transport of these emissions between source and receptor is simulated mathematically (Cramer and Bowers, 1980) to provide estimates of expected contributions.

This source-oriented method has the following limitations:

- Emission factors are inaccurate and variable.
- Many sources of particulate matter emissions are unidentified.
- Source models cannot adequately represent the deposition of particulate matter from the atmosphere.
- Source models cannot adequately represent the chemical and physical transformations of particles and gases.

The receptor model approach to estimating size-classified suspended particulate matter concentrations involves simultaneous size-classified and HIVOL sampling at representative receptors, the establishment of a relationship between size-classified concentrations and HIVOL concentrations (this is the receptor model), and an evaluation of the precision of this model in predicting size-classified concentrations at receptors similar to those from which the model was derived. Once formulated and validated, this model could be used to estimate size-classified concentrations with a definable uncertainty at receptors with HIVOL measurements.

The advantages of this receptor model approach are that it overcomes the limitations of the source-model method: no emission rate estimates, source identification, deposition rates, or chemical reaction mechanisms are required. The disadvantage is that the receptor model formulated for one receptor may not be applicable to another receptor. The relevant receptor characteristics which affect the transferability of the model must be identified in its formulation.

Any receptor model must be derivable from a source model to be physically significant. The starting point for the receptor model relating size-classified particulate matter concentrations to TSP concentrations is the typical urban mass distribution as a function of particle size (Willeke and Whitby, 1975) which is reproduced in Figure 8.1.1. If an aerosol sampler has an upper particle size cutpoint of D_c, the area under the distribution between 0 and D_c will be proportional to the ambient concentration measured by that sampler.

If two samplers with different cut-sizes, D_{c_1} and D_{c_2}, as illustrated in Figure 8.1.1, sample from the same size distribution, i, simultaneously, then the ratio of the concentrations, C_{1i} and C_{2i}, they measure will be proportional to the ratio of the areas indicated in Figure 8.1.1.

$$R_i = \frac{C_{2i}}{C_{1i}} = \frac{A_{2i}}{A_{1i}} \qquad 8\text{-}1$$

This assumes all other sampling biases (e.g. artifact formation) are negligible. If the particle size distributions for all samples, i=1.....n, retain the same shape, R_i will be the same for all i. In

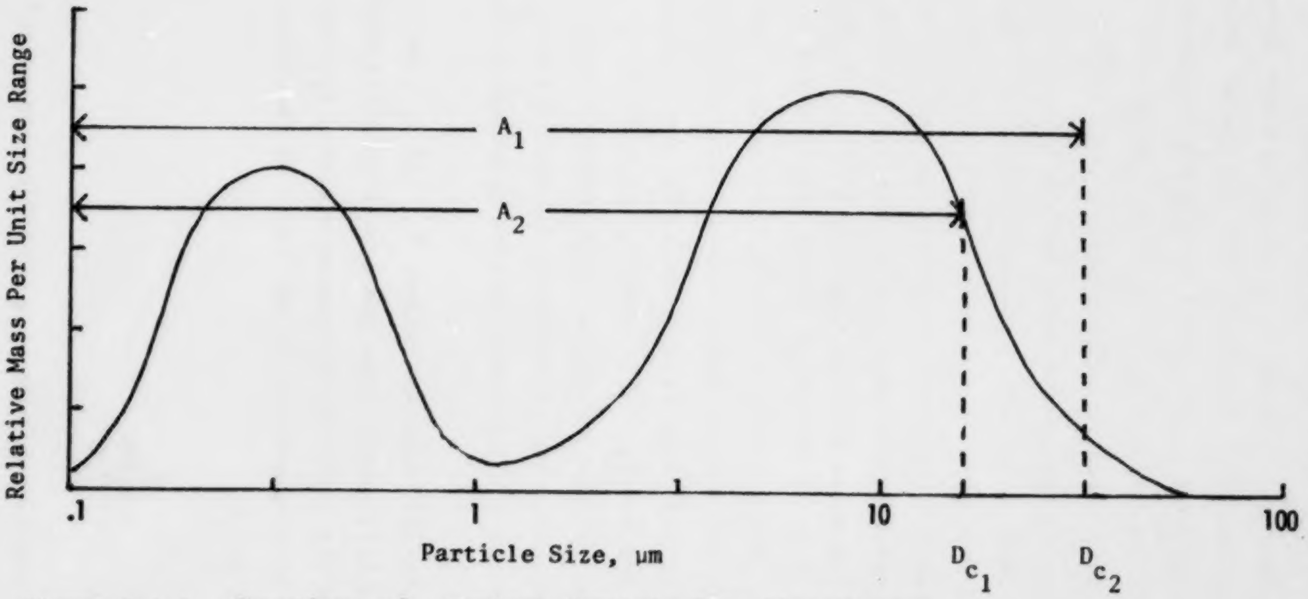


Figure 8.1.1 Fractions of a Typical Particle Size Distribution Collected by Sampler 1 and Sampler 2. This diagram is for illustrative purposes and is only one of many size distributions possible.

reality, the shapes of the size distributions will vary from sample to sample, and so will R_i. Sampler-specific biases, some of which were identified and estimated in Chapter 2, will also cause R_i to vary. The receptor model must include easily identifiable conditions which will minimize the variability of the size distribution and biases between samples and thereby reduce the variability of R_i.

Since the R_i are variable, the best estimate of one R for a set of samples must be a statistic which is a function of the R_i. Two simple statistics are available, the slope, $\overline{R}_L$, of a linear regression between C_1 and C_2 and an average of the individual ratios, $\overline{R}_A$.

The linear regression slope formulation modifies Equation 8-1 by adding a constant, b. Thus, an estimated concentration in size range 2, C_{2i}, as a function of the concentration in size range 1, C_{1i}, will be:

$$C_{2i} = \overline{R}_L C_{1i} + b \qquad 8\text{-}2$$

The values of $\overline{R}_L$ and b and the correlation coefficient, r, are (Bevington, 1969):

$$\overline{R}_L = \frac{\overline{C_2 \cdot C_1} - \overline{C}_1 \cdot \overline{C}_2}{\overline{C_1^2} - \overline{C}_1^2} \qquad 8\text{-}3$$

where

$$\overline{C_2 \cdot C_1} = \frac{1}{n} \sum_{i=1}^{n} C_{1i} C_{2i} \qquad 8\text{-}4$$

$$\overline{C} = \frac{1}{n} \sum_{i=1}^{n} C_i \qquad 8\text{-}5$$

$$\overline{C^2} = \frac{1}{n} \sum_{i=1}^{n} C_i^2 \qquad 8\text{-}6$$

$$b = \overline{C}_2 - \overline{R}_L\overline{C}_1 \qquad 8\text{-}7$$

$$r = \frac{\overline{C_2 \cdot C_1} - \overline{C}_1 \cdot \overline{C}_2}{(\overline{C_1^2} - \overline{C}_1^2)^{1/2} \cdot (\overline{C_2^2} - \overline{C}_2^2)^{1/2}} \qquad 8\text{-}8$$

Since IP and FP concentrations must equal zero when TSP goes to zero, b should be equal to zero. Due to measurement uncertainties, b can differ from zero, but it should be within a few times the lower quantifiable limit of zero.

The correlation coefficient (r) is indicative of the strength of the relationship between C_1 and C_2. For the purposes of this application, a correlation coefficient in excess of .9 means that the linear approximation is a good one; if r is less than .9, then the correspondence between the two variables is considered to be low and the independent variable is not deemed to be a good predictor of the dependent variable -- the receptor model is therefore an inaccurate representation of reality.

The other statistic is the arithmetic average of the ratios

$$\overline{R}_A = \frac{1}{n} \sum_{i=1}^{n} R_i \qquad 8\text{-}9$$

The standard deviation of the set of n R_i values,

$$\sigma_R = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (R_i - \overline{R}_A)^2} \qquad 8\text{-}10$$

is the best measure of the precision associated with estimates made from the relationship:

$$\hat{C}_{2i} = \bar{R}_A \cdot C_{1i} \qquad 8\text{-}11$$

The lower σ_R, the more precise will be the estimate $\hat{C}_{2i}$.

Trijonis et al (1980) applied the linear regression model of Equation 8-2 and the average ratio model of Equation 8-11 to HIVOL and TOTAL data acquired from simultaneous sampling with HIVOL and dichotomous samplers in St. Louis, Missouri during the 1976 Regional Air Monitoring Study (RAMS). The dichotomous samplers used in this program were of an earlier make (Loo and Jaklevic, 1974) and the upper size cutoff has been estimated at a larger size than that of the dichotomous samplers used in the IP Network. At the ten sites he considered, Trijonis found $\bar{R}_L$ varying between .20 and .74 for the TOTAL/HIVOL relationship and between .11 and .26 for the FINE/HIVOL relationship. The correlation coefficients ranged from .42 to .88 and .29 to .59 for TOTAL/HIVOL and FINE/HIVOL, respectively. Trijonis conclusion was that "...TSP measurements alone cannot adequately explain the day-to-day fluctuations in TOTAL... and FINE."

Trijonis et al (1980) also calculated average ratios, $\bar{R}_A$, and standard deviations, σ_R, for TOTAL/HIVOL at each of the RAMS sites. These average ratios at each site contained from 53 to 84 data pairs and ranged from .49 to .71 with standard deviations between .17 and .31. The overall ratio for all sites was .61 with a standard deviation of .22. Trijonis conclusion was that in the case of St. Louis, "...(HIVOL) is a poor predictor (of TOTAL) on a daily basis." Trijonis et al stratified their sample with respect to position, time and meteorology and found that for TOTAL/HIVOL the estimates of the average ratio were not substantially refined by this stratification.

These conclusions about the IP prediction receptor models applied to the RAMS data base are discouraging. They do not show a definitive relationship between IP or FP and TSP measurements. The data set used was limited, however, and it may be premature to dismiss the utility of the receptor models before exploring their applicability to a more complete set of measurements.

8.2 Site Type and Concentration Stratification

The IP Network provides the best set of simultaneous size-classified and TSP measurements for formulating and evaluating such a model. The sampling sites encompass a wide variety of land uses, which were identified in Chapter 3. The measurements are numerous enough that a wide range of concentrations for TSP, IP and FP concentrations are available. Each of these easily identifiable characteristics of samples could have an effect on the homogeneity of the particle size distribution within a sample set.

To form the receptor model, FINE, TOTAL, SSI, and HIVOL mass concentrations were used in Equations 8-3 and 8-7 to calculate the slope, $\overline{R}_L$, and intercept, b, of the linear regression formulation and in Equations 8-9 and 8-10 to calculate the average ratio, $\overline{R}_A$, and the standard deviation, σ_R, of the data set used to achieve it.

This was done for various groupings of data which were expected to have sampled size distributions which were more similar to each other than to the distributions sampled by the data base as a whole.

The following groupings were chosen:

- all data,
- site type classification, and
- HIVOL concentrations above and below 100 ug/m^3.

Both the linear regression slope and the average ratio models were applied to each group of measurements. These models were used to relate FINE, TOTAL and SSI concentrations to HIVOL measurements. The results of this sample stratification appear in Tables 8.2.1, 8.2.2, and 8.2.3 with stratifications by site type and concentration.

In deciding between which of two equally valid theories applies to a complex situation, the simpler one is that which should be chosen. Given the choice between the linear regression slope model and the average ratio model with both showing equal predictive ability, the average ratio model would be chosen because it is simpler to calculate and does not contain the constant, b, of the linear regression slope model.

TABLE 8.2.1

RECEPTOR MODEL EVALUATION OF SSI CONCENTRATIONS AS A FUNCTION OF HIVOL CONCENTRATIONS FOR DATA SETS STRATIFIED BY SITE TYPE AND HIVOL CONCENTRATION

Site Type	HIVOL Concentration Range (ug/m^3)	Arith. Average Ratio $\bar{R}_A \pm \sigma_R$	Linear Regression			Prediction Error Frequency Distribution		No. of Data Pairs	Arith.Avg.(ug/m^3)[a]	
			$\bar{R}_L \pm \sigma_R$	$b \pm \sigma_b$	r	Average Ratio	Linear Regression		HIVOL	SSI
All Sites	0 to 100	.74 ± .14	.70 ± .02	1.9 ± 1.0	.89	44,34,12,05,02,03	44,34,12,04,03,03	525	54.3	46.0
	100 to 300	.68 ± .13	.60 ± .04	10.5 ± 5.3	.80	42,27,18,04,03,04	41,30,18,04,03,04	158	142.2	97.0
	0 to 300	.72 ± .13	.64 ± .01	5.2 ± .9	.93	43,34,13,04,03,04	43,33,13,04,03,05	683	70.3	56.4
Urban Industrial (11)	0 to 100	.74 ± .13	.63 ± .03	6.0 ± 1.6	.87	41,37,13,04,02,02	47,32,13,03,01,04	216	60.0	46.9
	100 to 300	.66 ± .14	.50 ± .05	22.1 ± 6.8	.79	27,36,21,12,01,03	28,39,16,11,03,04	75	143.7	92.5
	0 to 300	.72 ± .13	.58 ± .02	9.9 ± 1.4	.91	39,34,16,03,05,03	43,32,14,07,01,04	291	80.2	57.8
Urban Commercial (12)	0 to 100	.74 ± .12	.71 ± .03	1.1 ± 1.7	.89	46,34,11,05,01,03	49,30,11,05,01,03	167	54.7	42.5
	100 to 300	.70 ± .11	.80 ± .08	-9.1 ± 12.4	.88	48,33,15,00,00,04	59,22,15,00,00,04	27	139.1	102.2
	0 to 300	.73 ± .12	.72 ± .02	.9 ± 1.5	.94	46,34,10,05,01,03	46,34,11,05,02,03	194	64.1	50.3
Urban Residential (13)	0 to 100	.69 ± .13	.89 ± .09	12.2 ± 6.0	.92	33,48,14,00,00,05	43,33,19,00,00,05	21	53.8	47.2
	100 to 300	.70 ± .12	.65 ± 11	6.9 ± 18.4	.85	75,08,08,00,00,08	75,08,08,00,00,08	12	145.2	108.2
	0 to 300	.69 ± .13	.69 ± .04	.4 ± 4.4	.95	48,33,12,00,00,06	48,33,12,00,00,06	33	67.5	67.0
Suburban Industrial (21)	0 to 100	.67 ± .07	.81 ± .07	2.8 ± 5.6	.99	78,11,00,11,00,00	67,22,11,00,00,00	9	65.4	56.2
	100 to 300	.66 ± .08	.56 ± .11	14.0 ± 16.6	.75	67,28,00,00,00,00	61,33,00,00,00,00	18	140.0	93.4
	0 to 300	.66 ± .09	.62 ± .05	4.6 ± 6.3	.92	70,22,00,04,00,04	63,30,00,04,04,00	27	96.9	70.1
Suburban Commercial (22)	0 to 100	.68 ± .12	.80 ± .09	-6.9 ± 6.1	.88	55,27,05,05,05,05	50,36,00,00,05,09	22	59.5	42.8
	100 to 300	.73						1	114.4	76.4
	0 to 300	.68 ± .12	.80 ± .08	-7.0 ± 5.5	.90	52,30,04,04,04,04	52,35,00,00,04,09	23	65.2	44.1
Suburban Residential (23)	0 to 100	.77 ± .21	.80 ± .03	- 2.1 ± 2.0	.94	51,27,07,09,02,04	52,25,10,09,02,02	81	51.6	46.1
	100 to 300	.79 ± .13	1.02 ± .12	-38.0 ± 16.7	.91	60,27,00,00,07,07	53,33,00,07,00,07	15	144.5	109.4
	0 to 300	.77 ± .20	.84 ± .02	-4.2 ± 1.9	.96	52,27,06,08,02,04	53,22,16,04,02,03	96	69.8	54.2
Rural Agricultural (34)	0 to 100							0	39.1	22.7
	100 to 300							0	140.1	
	0 to 300							0	53.1	22.7
Rural Remote (35)	0 to 100							0	27.7	
	100 to 300							0		
	0 to 300							0	27.7	

[a] Averages of paired measurements.

TABLE 8.2.2

RECEPTOR MODEL EVALUATION OF TOTAL CONCENTRATIONS AS A FUNCTION OF HIVOL CONCENTRATIONS FOR DATA SETS STRATIFIED BY SITE TYPE AND HIVOL CONCENTRATION

Site Type	HIVOL Concentration Range (ug/m^3)	Arith. Average Ratio $\bar{R}_A \pm \sigma_R$	Linear Regression $\bar{R}_L \pm \sigma_R$	Linear Regression $b \pm \sigma_b$	Linear Regression r	Prediction Error Frequency Distribution: Average Ratio	Prediction Error Frequency Distribution: Linear Regression	No. of Data Pairs	Arith.Avg.(ug/m^3)^a HIVOL	Arith.Avg.(ug/m^3)^a SSI
All Sites	0 to 100	.75 ± .18	.62 ± .01	5.5 ± .8	.83	32,28,22,08,04,08	32,29,20,08,04,07	952	54.3	39.2
	100 to 300	.63 ± .14	.68 ± .04	-7.5 ± 5.7	.79	32,27,26,10,03,02	31,29,25,09,04,02	183	142.2	87.1
	0 to 300	.73 ± .18	.60 ± .01	5.3 ± .7	.90	32,25,22,08,05,07	31,30,21,08,05,06	1135	70.3	45.0
Urban Industrial (11)	0 to 100	.76 ± .14	.68 ± .03	4.4 ± 1.8	.86	41,33,15,05,03,03	43,33,13,05,03,03	196	60.0	44.5
	100 to 300	.68 ± .13	.65 ± .07	4.5 ± 9.3	.78	37,32,16,11,03,02	33,35,14,11,06,00	63	143.7	92.0
	0 to 300	.74 ± .14	.63 ± .02	6.8 ± 1.5	.91	42,28,17,06,04,03	40,32,14,07,03,03	259	80.2	52.7
Urban Commercial (12)	0 to 100	.72 ± .18	.52 ± .03	9.6 ± 1.9	.74	26,28,24,08,06,08	31,28,20,08,05,08	215	54.7	40.5
	100 to 300	.58 ± .12	.62 ± .07	7.6 ± 9.9	.85	26,35,24,15,00,00	38,26,21,15,00,00	34	139.1	80.2
	0 to 300	.70 ± .18	.54 ± .02	8.4 ± 1.5	.87	22,29,24,10,06,09	31,28,21,10,04,06	249	64.1	44.9
Urban Residential (13)	0 to 100	.78 ± .17	.72 ± .05	2.5 ± 2.8	.84	40,29,13,09,04,06	38,29,16,09,04,05	80	53.8	38.2
	100 to 300	.66 ± .21	.65 ± .23	1.5 ± 32.8	.73	29,00,14,43,14,00	29,00,14,43,14,00	7	145.2	90.3
	0 to 300	.77 ± .18	.64 ± .04	6.2 ± 2.3	.88	40,24,15,09,02,09	37,26,18,03,09,06	87	67.5	41.9
Suburban Industrial (21)	0 to 100	.59 ± .10	.54 ± .09	3.0 ± 6.1	.86	40,27,27,07,00,00	40,33,20,07,00,00	15	65.4	46.7
	100 to 300	.55 ± .09	.14 ± .13	56.4 ± 17.6	.29	46,46,00,00,08,00	54,38,08,00,00,00	13	140.0	75.6
	0 to 300	.57 ± .09	.47 ± .04	9.2 ± 4.6	.90	39,39,18,00,04,00	46,36,07,04,07,00	28	96.9	54.7
Suburban Commercial (22)	0 to 100	.64 ± .18	.52 ± .07	6.6 ± 4.1	.69	20,26,22,15,08,09	20,28,20,14,09,09	65	59.5	38.0
	100 to 300	.61 ± .15	.55 ± .38	6.9 ± 42.6	.51	50,17,17,17,00,00	50,00,33,17,00,00	06	114.4	68.7
	0 to 300	.64 ± .18	.55 ± .05	5.0 ± 3.0	.78	21,25,24,14,07,08	23,30,15,18,06,08	71	65.2	40.1
Suburban Residential (23)	0 to 100	.75 ± .15	.70 ± .02	1.9 ± 1.2	.88	32,33,22,05,02,06	35,33,22,05,02,06	277	51.6	37.6
	100 to 300	.61 ± .13	.85 ± .08	5.9 ± 9.8	.83	33,29,21,08,06,02	38,27,19,08,04,04	48	144.5	91.8
	0 to 300	.73 ± .16	.63 ± .02	4.5 ± 1.2	.91	34,27,22,06,05,06	32,30,21,07,04,06	325	69.8	43.3
Rural Agricultural (34)	0 to 100	.84 ± .28	.63 ± .04	6.8 ± 2.0	.86	32,36,08,06,08,09	30,27,21,05,04,13	77	39.1	31.1
	100 to 300	.60 ± .12	.53 ± .11	8.7 ± 15.0	.84	36,36,18,00,00,09	36,45,09,00,00,09	11	40.1	81.7
	0 to 300	.81 ± .28	.55 ± .03	9.5 ± 1.7	.92	31,34,07,13,07,09	32,23,19,08,03,15	88	53.1	36.5
Rural Remote (35)	0 to 100	.91 ± .26	.87 ± .34	.8 ± 8.3	.76	40,20,20,00,00,20	40,20,20,00,00,20	5	27.7	12.5
	100 to 300					00,00,00,00,00,00	00,00,00,00,00,00	0		
	0 to 300	.91 ± .26	.87 ± .34	.87 ± 8.3	.76	40,20,20,00,00,20	40,20,20,00,00,20	5	27.7	12.5

[a] Averages of paired measurements.

TABLE 8.2.3

RECEPTOR MODEL EVALUATION OF FINE CONCENTRATIONS AS A FUNCTION OF HIVOL CONCENTRATIONS FOR DATA SETS STRATIFIED BY SITE TYPE AND HIVOL CONCENTRATION

Site Type	HIVOL Concentration Range	Arith. Average Ratio	Linear Regression			Prediction Error Frequency Distribution		No. of Data	Arith.Avg.(ug/m^3)[a]	
	(ug/m^3)	$\bar{R}_A \pm \sigma_R$	$\bar{R}_L \pm \sigma_R$	$b \pm \sigma_b$	r	Average Ratio	Linear Regression	Pairs	HIVOL	SSI
All Sites	0 to 100	.42 ± .19	.29 ± .02	6.0 ± .8	.53	18,16,18,13,07,28	15,17,18,13,09,27	952	54.3	21.7
	100 to 300	.28 ± .14	.24 ± .04	5.9 ± 6.4	.38	11,12,14,16,12,36	10,12,16,15,10,36	183	142.2	38.5
	0 to 300	.40 ± .19	.23 ± .01	8.9 ± .7	.59	17,15,17,14,08,29	16,13,18,13,10,30	1135	70.3	23.7
Urban Industrial (11)	0 to 100	.45 ± .15	.32 ± .03	6.2 ± 1.8	.62	25,19,21,09,08,19	23,27,17,10,06,08	196	60.0	24.9
	100 to 300	.33 ± .13	.29 ± .07	5.8 ± 9.8	.46	27,36,21,12,01,03	28,39,16,11,03,04	75	143.7	44.8
	0 to 300	.42 ± .15	.27 ± .02	9.0 ± 1.6	.68	22,19,16,14,07,23	20,26,17,11,07,09	259	80.2	28.4
Urban Commercial (12)	0 to 100	.38 ± .18	.25 ± .03	6.3 ± 2.1	.44	11,13,17,19,08,33	13,13,17,14,11,32	215	54.7	20.7
	100 to 300	.24 ± .13	.12 ± .08	10.0 ± 10.5	.27	12,12,15,12,12,58	09,15,12,09,12,41	34	139.1	32.4
	0 to 300	.36 ± .18	.17 ± .02	10.3 ± 1.6	.47	10,14,11,20,08,36	12,12,16,14,10,36	249	64.0	22.0
Urban Residential (13)	0 to 100	.47 ± .19	.40 ± .06	2.8 ± 3.2	.59	24,29,16,09,09,24	19,23,16,09,07,24	80	53.8	22.4
	100 to 300	.36 ± .21	.55 ± .27	29.0 ± 38.0	.62	14,14,00,00,29,43	00,29,00,00,14,57	7	145.2	50.9
	0 to 300	.46 ± .20	.37 ± .04	3.8 ± 2.7	.69	21,18,16,11,08,25	18,22,13,16,07,24	87	67.5	24.5
Suburban Industrial (21)	0 to 100	.30 ± .10	.20 ± .09	6.0 ± 6.4	.50	13,40,07,20,00,20	13,20,40,07,00,20	15	65.4	25.1
	100 to 300	.21 ± .08	-.03 ± .14	32.7 ± 19.2	-.06	46,15,00,08,15,15	08,23,15,38,00,15	13	140.0	28.9
	0 to 300	.26 ± .10	.12 ± .04	11.6 ± 4.4	.50	14,11,29,18,14,14	18,29,14,11,11,08	28	96.9	26.1
Suburban Commercial (22)	0 to 100	.32 ± .18	.22 ± .07	5.7 ± 4.0	.38	09,09,09,15,15,42	11,08,11,09,25,37	65	59.5	19.7
	100 to 300	.31 ± .18	.08 ± .46	26.0 ± 52.3	.06	33,00,00,00,00,67	17,17,17,00,00,50	06	114.4	34.4
	0 to 300	.32 ± .18	.25 ± .05	4.3 ± 3.7	.47	10,10,08,14,15,15	10,11,10,10,23,37	71	65.2	20.7
Suburban Residential (23)	0 to 100	.45 ± .17	.37 ± .03	3.2 ± 1.4	.66	25,17,13,10,09,20	21,18,20,12,18,20	277	51.6	22.1
	100 to 300	.27 ± .13	.35 ± .08	28.9 ± 11.5	.55	13,21,13,10,15,29	17,06,23,10,21,23	48	144.5	40.5
	0 to 300	.43 ± .18	.25 ± .02	8.3 ± 1.2	.67	20,15,16,16,08,25	16,17,19,12,11,26	325	69.8	24.1
Rural Agricultural (34)	0 to 100	.46 ± .27	.12 ± .05	10.9 ± 2.2	.37	09,17,19,10,06,38	14,04,12,09,17,44	77	39.1	15.4
	100 to 300	.13 ± .10	-.10 ± .06	28.5 ± 9.0	-.42	27,09,09,09,10,45	09,27,09,00,18,36	11	140.1	15.4
	0 to 300	.41 ± .28	.02 ± .03	14.3 ± 1.7	.09	09,10,18,09,13,41	14,07,10,03,16,50	88	53.1	15.4
Rural Remote (35)	1 to 100	.61 ± .16	.68 ± .20	1.3 ± 4.9	.84	20,40,20,00,20,00	20,60,00,00,00,20	5	27.7	9.2
	100 to 300									
	0 to 300	.61 ± .16	.68 ± .20	1.3 ± 4.9	.84	20,40,20,20,20,00	20,60,00,00,00,20	5	27.1	9.2

[a] Averages of paired measurements.

Similarly, given equal predictive power and the choice between a model requiring stratified data sets and one without stratification, the one without stratification would be simpler and therefore more desirable.

The key question to be answered is that of equal predictive power. Two criteria have already been advanced and one more is proposed. One model will be a better predictor than another model if:

- the standard deviation of the average ratio is significantly reduced by stratification,
- the correlation coefficient of the linear regression slope model is significantly increased, and
- the distribution of percent differences between predicted and measured values is shifted to the lower percent differences.

For each pair of data points represented in Tables 8.2.1 to 8.2.3, the absolute value of the relative difference, d_i, between the measured and predicted values has been calculated from:

$$d_i = \left| \frac{C_{2i} - \hat{C}_{2i}}{C_{2i}} \right| \qquad 8\text{-}12$$

and the fraction of the d_i in the intervals 0 to .1, .1 to .2, .2 to .3, .3 to .4, .4 to .5, and greater than .5 have been totaled. These distributions were formed for each stratified set of data for both the linear regression slope, and the average ratio receptor models. Figure 8.2.1 illustrates the distribution drawn from the comparison of SSI concent$\hat{r}$ations calculated from the linear regression model with the measurements for all sites in the 0 to 300 ug/m^3 HIVOL concentration range. This histogram reflects the set of six numbers (43, 33, 13, 4, 3, 5) taken from the third row and eighth column of Table 8.2.1. Every set of six numbers in columns 7 and 8 of Tables 8.2.1, 8.2.2 and 8.2.3 can be interpreted in the same way. For example, of the 683 predicted SSI concentrations from the linear regression receptor model, the set of numbers in column 8 states that

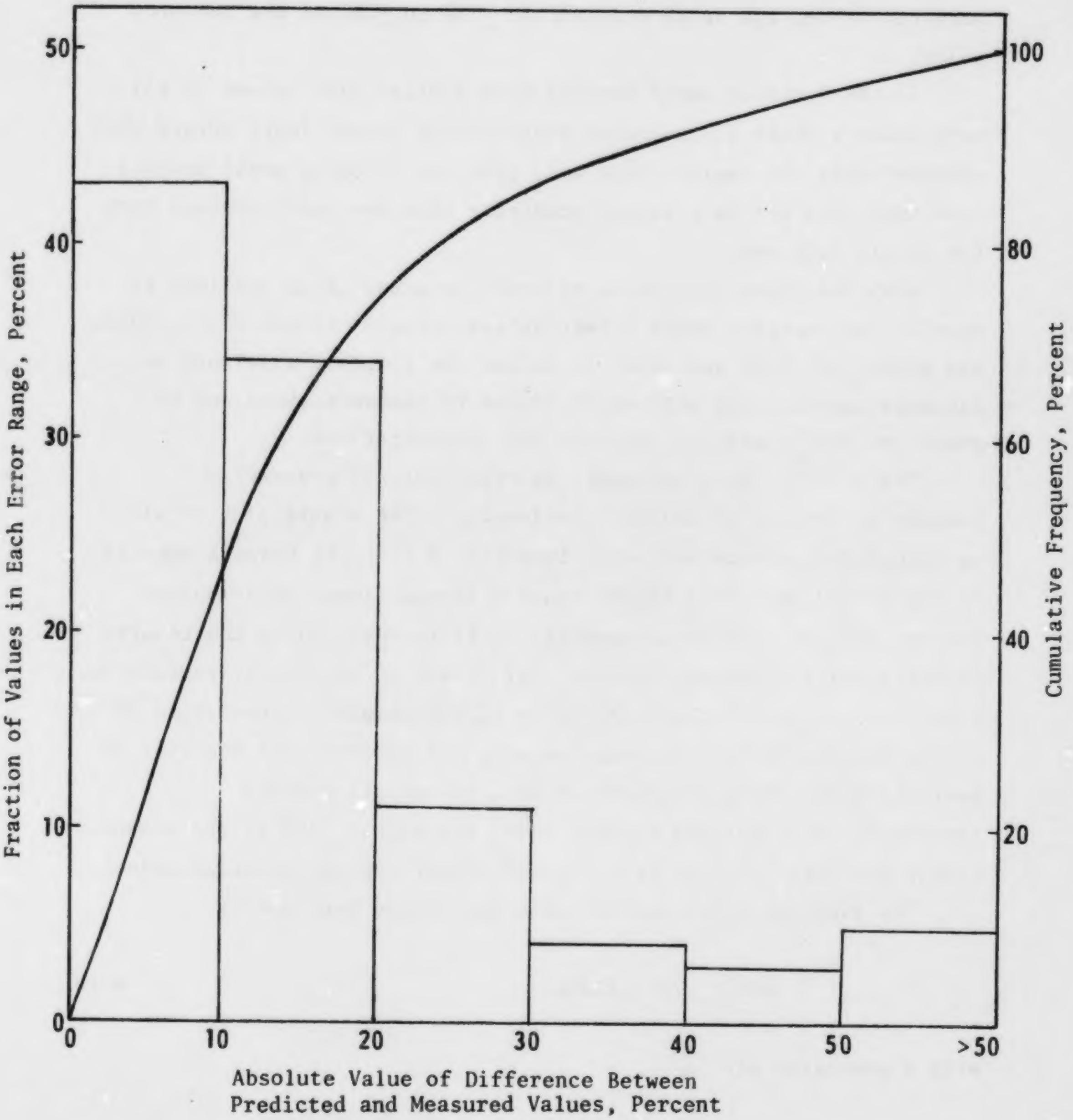


Figure 8.2.1 Frequency Distribution of relative differences between SSI predicted and measured concentrations calculated from the Linear Regression Slope Model for all sites.

43%, or 294 of those predictions were within ±10% of the measured value, 33% or 225 of the predictions were within ±10% to ±20% of the measured value, 13% or 89 were within ±20% to ±30% of the measured value, etc.

If the receptor model derived from a stratified subset of all data shows a shift in the error distribution toward lower errors when compared with the overall data set, then the receptor model derived from that data set is a better predictor than the model derived from the entire data set.

With the three evaluation criteria in mind, it is possible to examine the receptor model relationships between SSI and HIVOL, TOTAL and HIVOL, and FINE and HIVOL to define the simplest model and to estimate the accuracy with which IP and FP concentrations can be predicted from routinely acquired TSP concentrations.

Table 8.2.1 shows the model calculations and evaluation parameters for the SSI/HIVOL relationship. The scatterplot of all validated data points available from the IP Sampling Network appears in Figure 8.2.2a. This figure shows a strong linear relationship between SSI and HIVOL measurements. This is verified by the results in Table 8.2.1. The correlation coefficient of the linear regression model is .93 (recall that collocated HIVOLs showed a correlation of .98 in Section 3.5). The relative standard deviation of the average ratio is ±18%. Most important of all, 90% of all the SSI concentrations predicted by this model are within ±30% of the measured values for both the average ratio and linear regression slope models.

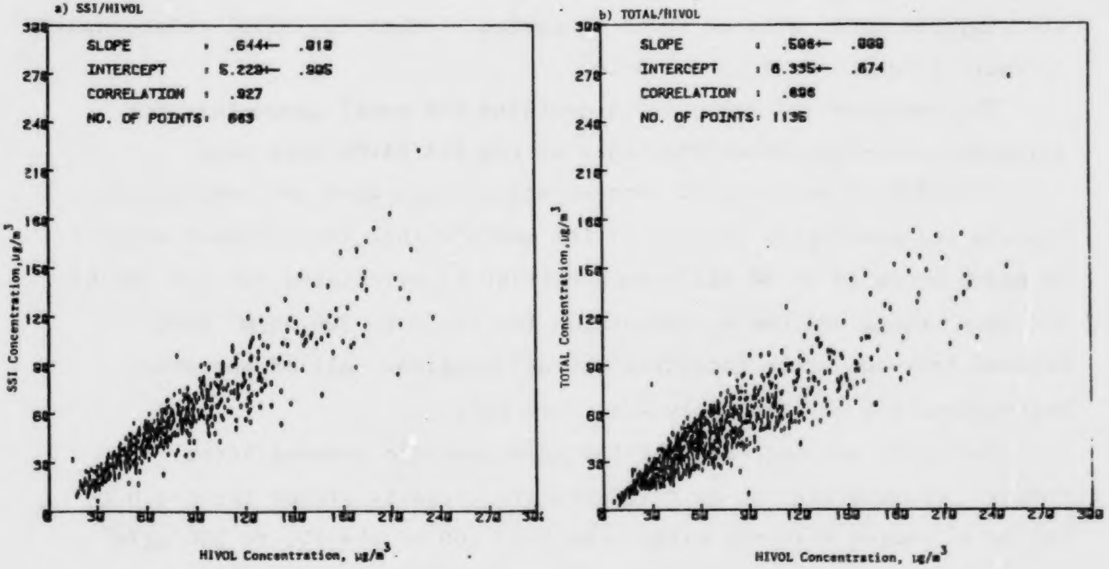
The simplest model derived from the entire data set is

$$\mathrm{SSI} = .72 \times \mathrm{HIVOL} \qquad \text{8-13}$$

with a precision of

$$\sigma_{\mathrm{SSI}} = .13 \times \mathrm{HIVOL} \qquad \text{8-14}$$

Within the same data set, stratification by concentration does not offer any advantage. The standard deviation of the average ratio is not reduced by the stratification, and the average ratio itself changes by at most .04,


a) SSI/HIVOL

b) TOTAL/HIVOL

c) FINE/HIVOL

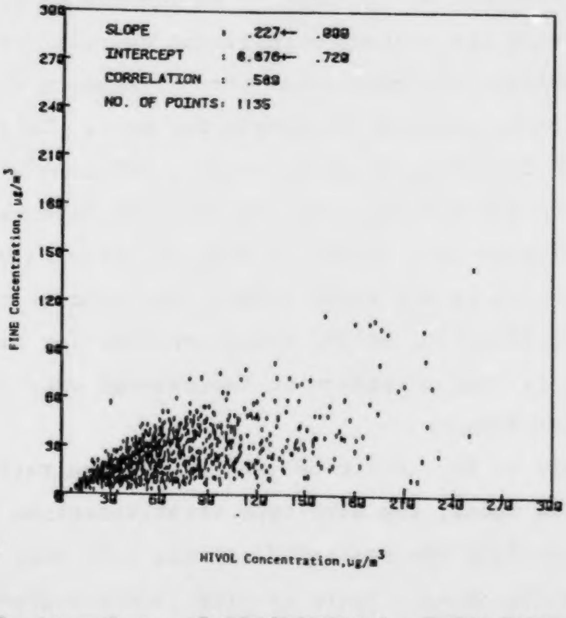


Figure 8.2.2a-c - Scatterplots of SSI/HIVOL(a), TOTAL/HIVOL(b), FINE/HIVOL(c) for all IP Network Sites, 0 to 300 µg/m^3 HIVOL Concentration Range.

or by less than 6%. The prediction error frequency distributions are not shifted to the lower percentages by the HIVOL concentration stratification. There is little difference between distributions resulting from the average ratio and the linear regression slope model. Therefore, the simplest model against which to evaluate other SSI/HIVOL relationships is that of Equations 8-13 and 8-14.

The remainder of Table 8.2.1 contains the model parameters for different site-type stratifications of the SSI/HIVOL data sets.

Stratification by HIVOL concentration range does not substantially improve the predictive ability of the model within any of these subsets. At most, there is an 8% difference between $\overline{R}_A$ calculated for the 100 to 300 ug/m^3 range and the $\overline{R}_A$ calculated for the 0 to 300 ug/m^3 range derived from the urban industrial stratification. All of the other differences are substantially less than this.

The σ_R do not decrease for the more specific concentration ranges. The correlation coefficients are actually higher for the 0 to 300 ug/m^3 ranges than for either the 0 to 100 or the 100 to 300 ug/m^3 ranges. (This is more a function of sample size and range of data values than of an improvement in the model. As the number of points in a sample increases, so does the minimum significant correlation coefficient.)

Most important, the prediction error frequency distributions between concentration range subsets are nearly the same. Only the urban residential 100 to 300 ug/m^3 range shows a substantial shift from the 10 to 20% and 20 to 30% intervals to the 0 to 10% interval. Because the number of samples in this subset is only 12, this only represents shifts of a few samples which is not significant. The conclusion to be drawn with respect to stratification by TSP concentrations for predicting SSI concentrations is that it offers no improvement over the model formed from the unstratified data.

With regard to the choice between an average ratio and a linear regression slope model, the site-type stratifications confirm the conclusion drawn from the unstratified data set, that one model is as good a predictor as the other. There is very little difference between the prediction error frequency distributions of either model applied to the same data set. Thus, within each stratified data set, the average ratio without TSP concentration stratification is the simplest receptor model.

Comparing these average ratios between site-type stratifications shows little difference between the average ratio calculated from all sites and the average ratios determined from sample stratification. The average ratios range from .66 to .77, a maximum deviation of 7% from the value of .72 for all sites. Only in the suburban industrial case is the standard deviation of the average appreciably smaller than that for all sites, but since so few samples are in this subset, this reduction is probably insignificant.

The conclusion of this analysis is that the best receptor model for the prediction of SSI concentrations from HIVOL measurements is that of Equations 8-13 and 8-14. A caveat is important here. Four hundred, or 59%, of the data points in the "all sites" sample come from Philadelphia, and most of the sites in this area are of the urban industrial type. The model is heavily influenced by them. Even though a variety of site classifications is represented, the particle size distributions which were sampled in Philadelphia may be more similar to each other than they are to particle size distributions in different cities.

The relationship between TOTAL and HIVOL may be a more representative receptor model to predict IP from TSP because the number of simultaneous TOTAL/HIVOL measurements is nearly twice as great and the measurements are more uniformly distributed throughout the network than are the SSI/HIVOL pairs. It's predictive ability may suffer, however, because of the change in filter media from 1979 to 1980 which was shown in Chapter 3 to induce a potential mass bias under certain conditions. This relationship is examined in Table 8.2.2.

Figure 8.2.2b shows the scatterplot of TOTAL/HIVOL pairs. Though a linear relationship is discernible, it is not as strong as the one in Figure 8.2.2a. The correlation coefficient of .90 is still fairly high, however, indicating that a linear model is a reasonable approximation.

Both the linear regression and the average ratio models predict TOTAL concentrations within ±30% of the measured values for 80% of the data pairs. This pattern holds true through all of the stratified data sets. There is, therefore, no reason to choose the more complicated linear regression slope model over the average ratio model. This model shows less prediction accuracy than the corresponding SSI/HIVOL model.

Stratification by HIVOL concentration has a more significant effect on the TOTAL/HIVOL relationship than it does on the SSI/HIVOL relationship. This is consistent with the cumulative frequency distributions of the TOTAL and SSI concentrations examined in Chapter 7. Figure 7.2.1c shows a horizontal tendency for the high concentrations for the TOTAL samples while the SSI (Figure 7.2.1b) distribution continues to follow a straight line. This is possibly due to the loss of material from the COARSE filters. This difference between the 0 to 100 ug/m^3 and 100 to 300 ug/m^3 HIVOL concentration ranges appears to be significant in most of the stratified data sets. The suburban industrial and suburban commercial subsets show only small differences between average ratios for the concentration stratification, but since the number of samples in each 100 to 300 ug/m^3 category is small (less than 13), great significance should not be attached to this observation.

The average ratios in both the 0 to 100 ug/m^3 and 100 to 300 ug/m^3 ranges for the urban industrial, urban commercial, urban residential, and suburban residential site types differ by no more than 8% from those calculated from all sites. This is not surprising since 81% of the data pairs in all sites come from these four site types. The simplest model for these sites should be:

for HIVOL $< 100\ ug/m^3$

$$\text{TOTAL} = .75 \times \text{HIVOL} \qquad 8\text{-}15$$

$$\sigma_{\text{TOTAL}} = .18 \times \text{HIVOL} \qquad 8\text{-}16$$

for HIVOL $> 100\ ug/m^3$

$$\text{TOTAL} = .63 \times \text{HIVOL} \qquad 8\text{-}17$$

$$\sigma_{\text{TOTAL}} = .16 \times \text{HIVOL} \qquad 8\text{-}18$$

The suburban commercial category shows a very low correlation, .79, between TOTAL and HIVOL and it yields an average ratio which is 15% lower than the average ratio for all sites. The average ratio of .68 for the SSI/HIVOL relationship in Table 8.2.1 is also lower than that for all sites, but not to such a great extent. The poor correlation, the limited number of data pairs and the inconsistency with the SSI/HIVOL relationship for the same site-type stratification cast doubt on the use of a separate receptor model for the suburban commercial stratification.

The rural agricultural classification also shows a substantial increase in the average ratio with respect to the ratio for all sites, but the standard deviation of this ratio is large, indicating a great variability of this ratio. The prediction error frequency distribution for this classification shows the average ratio model to be a much better estimator than the linear regression model, though for the 0 to 300 ug/m^3 range, the correlation coefficient of .92 is higher than that for all sites. No SSI/HIVOL data is available for comparison. This site-type classification could be a legitimate alternative to Equations 8-15 and 8-16 (notice that for concentrations in the 100 to 300 ug/m^3 range, the average ratios and standard deviations are nearly identical for rural agricultural and all sites) but more confirmation is needed.

It appears, then, that the receptor model embodied in Equations 8-13 to 8-16 is the most reasonable one for predicting TOTAL concentrations from HIVOL concentrations. For HIVOL concentrations less than 100 ug/m^3, the TOTAL/HIVOL model is almost identical to the SSI/HIVOL model, with the average ratios differing by only 4%. For the HIVOL concentrations greater than 100 ug/m^3, however, there is a substantial difference.

Table 8.2.3 is the counterpart to Tables 8.2.1 and 8.2.2 for the relationship between FINE and HIVOL concentrations. The scatterplot of this relationship for all sites appears in Figure 8.2.2c. A strong linear relationship between these two measurements is not visually evident, and the low correlation coefficient of .59 confirms this lack of association.

As Table 8.2.3 shows, neither stratification by HIVOL concentration nor by site type increases the correlation between FINE and HIVOL to a significant level. The highest correlation (discounting the rural remote classification for which only five data points are available) is only .69, far below the .90 which was specified in the model evaluation criteria.

The prediction error frequency distributions consistently yield more than half of the predictions differing from measured values by more than ±30%, showing that none of the models can be relied upon to accurately estimate FINE concentrations from HIVOL concentrations.

It must be concluded from the results in Table 8.2.3 that the proposed receptor model is inadequate for predicting FINE concentrations from HIVOL measurements.

Average ratios, $\overline{R}_A$, for SSI/HIVOL and TOTAL/HIVOL from sites having at least 19 data pairs are plotted in Figure 8.2.3 where they have been stratified by site classification code. No HIVOL concentration stratification was used in calculating the ratios for TOTAL/HIVOL because the numbers of points in the 100 to 300 ug/m^3 range of individual sites were too low to make a calculated ratio significant. The average ratios, $\overline{R}_A$, and standard deviations, σ_R, drawn from Tables 8.2.1 and 8.2.2 have been placed on the graphs for comparison.

As indicated by the stratifications in Tables 8.2.1 and 8.2.2, a site-type classification is irrelevant to the relationship between IP and TSP. Apparently the particle size distributions are just as variable at rural and suburban sites as they are at urban sites. This does not imply that the distributions vary in the same way, but that the effect of those variations on the IP/TSP ratios is the same.

8.3 Predicting IP from TSP Concentrations

The average ratio model provides a reasonable prediction of SSI and TOTAL concentrations from HIVOL concentrations when the average ratio and standard deviation are calculated from the same data set for which the predictions are being made. In practice, if IP measurements were available, then there would be no need for a predictive model. To make this receptor model a practical predictor, it is necessary to demonstrate that the model derived from one set of SSI/HIVOL or TOTAL/HIVOL pairs can predict, with a given degree of accuracy, the SSI or TOTAL values associated with a set of HIVOL concentrations which had nothing to do with the formation of the receptor model. For example, given one year of SSI/HIVOL or TOTAL/HIVOL data at a site,

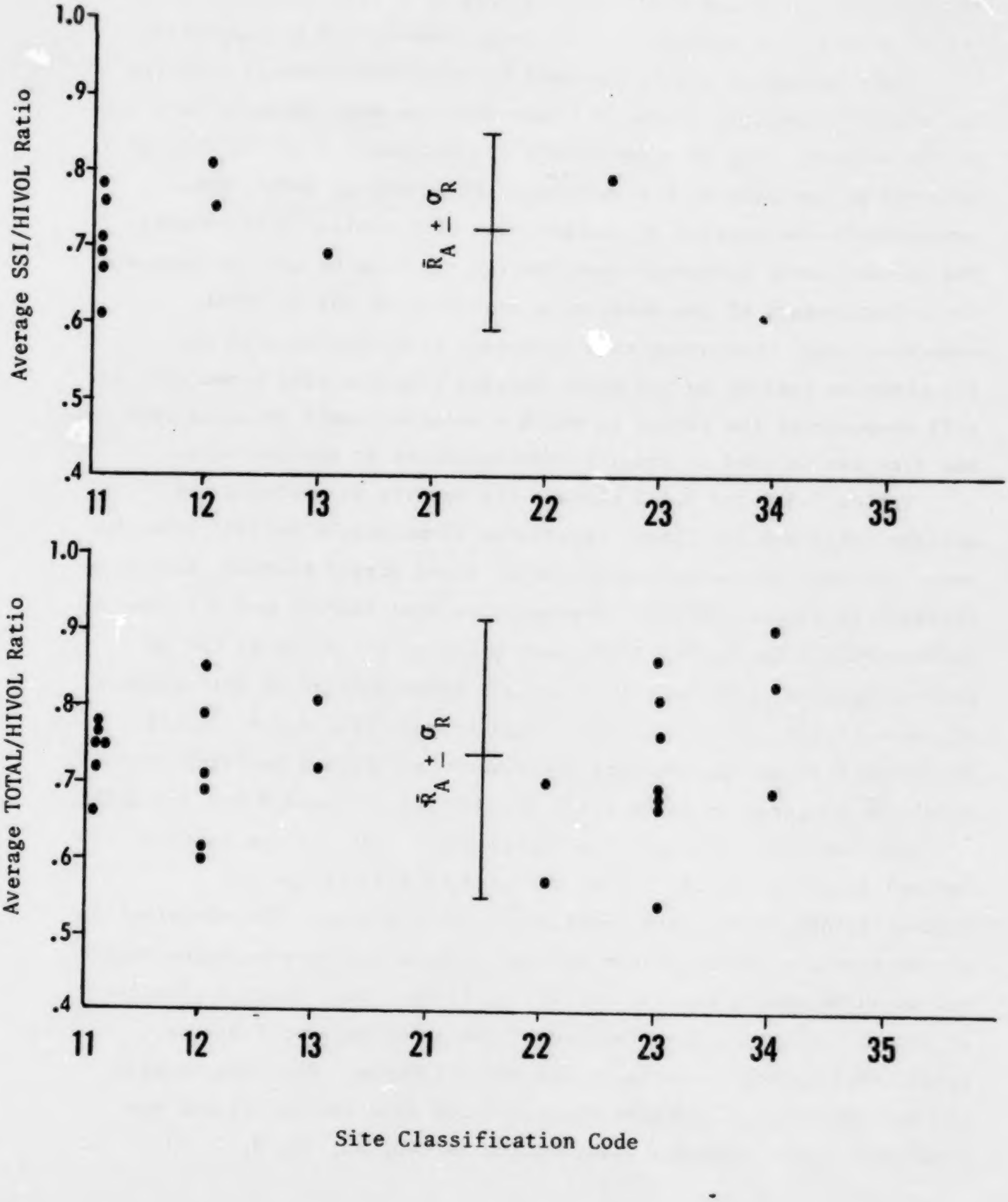


Figure 8.2.3 Average SSI/HIVOL and TOTAL/HIVOL Ratios at IP Network Sites

how well could one predict SSI or TOTAL at another site in the same vicinity or at a site in a completely different area? Given one year of simultaneous IP and HIVOL measurements at a site, how well could the IP values from the previous or later time period be predicted?

These questions can be answered by using measurements from the Philadelphia sampling sites, the ones with the most complete data sets in the network. The receptor models can be formed from the data pairs acquired at one site with simultaneous SSI/HIVOL or TOTAL/HIVOL measurements and applied at another site with similar measurements. The percent error frequency distribution can then be used to evaluate the effectiveness of the model as a predictor of SSI or TOTAL concentrations. Comparing this frequency distribution with the distribution yielded by the model derived from the site's own data set will demonstrate the extent to which a receptor model obtained from one site can be used to predict concentrations at another site.

Tables 8.3.1 and 8.3.2 contain the results of applying the average ratio and the linear regression slope models derived from the year-long data sets acquired at 500 S. Broad Street (PAPHA), Allegheny (PAPHB), NE Airport (PAPHE), Presbyterian Home (PAPHG) and St. John's Church (PAPHI) to the SSI/HIVOL data pairs of all sites in the IP Network outside of Philadelphia, to all sites outside of Philadelphia of one site-type classification (urban commercial), and to itself. The prediction error frequency distributions obtained by using each model are compared in Table 8.3.1 for SSI and in Table 8.3.2 for TOTAL.

For example, in column 4 of Table 8.3.1, the average ratio of .75 derived at 500 S. Broad (PAPHA) was used to predict the SSI concentrations at all sites outside of Philadelphia. The distribution of the absolute values of the percent differences between calculated and measured values is (43, 31, 12, 8, 1, 5). This distribution can be compared with the distribution of the model derived from the predicted data set to evaluate its effectiveness. For this example, the average ratio yielded by the predicted data set is .72 and the predicted error frequency distribution is (43, 33, 14, 3, 2, 4).

TABLE 8.3.1

PREDICTION ERROR FREQUENCY DISTRIBUTIONS USING SSI/HIVOL MODELS DERIVED FROM SINGLE SITES FOR VARIOUS DATA SETS NOT INCLUDED IN THE MODEL

Predicted Data Set	Predicted Data Set Model Parameters appear under data set headings in first column		Predicted Error Frequency Distributions 500 S. Broad (PAPHA) $\bar{R}_A$ = .75 $\bar{R}_L$ = .82 $\bar{b}$ = 3.40 n = 107		Allegheny (PAPHB) $\bar{R}_A$ = .67 $\bar{R}_L$ = .54 $\bar{b}$ = 11.80 n = 76		NE Airport (PAPHE) Insufficient data		Pres. Home (PAPHG) Insufficient data		St. John's (PAPHI) $\bar{R}_A$ = .78 $\bar{R}_L$ = .84 $\bar{b}$ = 3.5 n = 91	
	AVR[a]	LRS[b]	AVR	LRS	AVR	LRS	AVR	LRS	AVR	LRS	AVR	LRS
All Sites	43	42	43	41	40	36					40	37
but Philadephia	33	35	31	25	34	28					28	24
$\bar{R}_A$ = .72	14	14	12	19	18	15					14	18
$\bar{R}_L$ = .70	3	3	8	6	4	7					7	10
b = .59	2	2	1	3	1	3					4	5
n = 288	4	4	5	5	2	10					6	5
All Urban-Commercial	48	45	28	32	45	35					27	27
Sites Except Philadelphia	32	30	35	23	30	23					25	18
$\bar{R}_A$ = .66	8	15	15	22	13	18					22	27
$\bar{R}_L$ = .74	7	8	12	10	7	5					8	12
b = 5.70	2	0	2	5	2	8					8	8
n = 60	3	2	8	8	3	10					10	8
Own Site			57	51	32	39					55	52
Model parameters appear			27	36	32	31					31	35
under site name heading			10	9	18	19					8	8
in first row			3	1	10	4					2	3
			1	1	3	1					3	1
			2	2	4	5					1	1

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[a] AVR - Average Ratio Model

[b] LRS - Linear Regression Slope Model

[c] These six numbers represent the fraction of the predicted and observed IP value which differed from each other by 0 to 10%, 10 to 20%, 20 to 30%, 30 to 40%, 40 to 50%, and greater than 50%, respectively.

TABLE 8.3.2

PREDICTION ERROR FREQUENCY DISTRIBUTIONS USING TOTAL/HIVOL MODELS DERIVED FROM SINGLE SITES FOR VARIOUS DATA SETS NOT INCLUDED IN THE MODEL

Predicted Data Set	Predicted Data Set Model Parameters appear under data set headings in first column		Predicted Error Frequency Distributions 500 S. Broad (PAPHA) $\bar{R}_A$ = .79 $\bar{R}_L$ = .63 $\bar{b}$ = 8.80 n = 25		Allegheny (PAPHB) $\bar{R}_A$ = .81 $\bar{R}_L$ = .46 $\bar{b}$ = 17.70 n = 14		NE Airport (PAPHE) $\bar{R}_A$ = .81 $\bar{R}_L$ = .77 $\bar{b}$ = 1.40 n = 74		Pres. Home (PAPHG) $\bar{R}_A$ = .81 $\bar{R}_L$ = .81 $\bar{b}$ = 2.10 n = 48		St. John's (PAPHI) $\bar{R}_A$ = .78 $\bar{R}_L$ = .70 $\bar{b}$ = 3.50 n = 17	
	AVR[a]	LRS[b]	AVR	LRS	AVR	LRS	AVR	LRS	AVR	LRS	AVR	LRS
All Sites	27	31	24	25	27	23	23	24	23	22	24	26
but Philadephia Sites	27	25	23	21	27	23	22	23	21	19	24	24
$\bar{R}_A$ = .70	22	24	15	17	21	17	15	15	14	16	16	18
$\bar{R}_L$ = .58	11	9	11	11	15	9	12	10	12	12	11	11
$\bar{b}$ = 5.20	6	4	9	8	5	5	9	9	9	9	7	8
n = 780	7	6	18	18	5	22	19	18	29	22	17	14
All Urban-Commercial	25	30	24	23	25	21	23	23	23	22	24	27
Sites Except Philadelphia	29	27	16	22	28	23	16	17	16	14	19	18
$\bar{R}_A$ = .66 Sites	17	24	16	14	18	20	15	16	13	15	17	16
$\bar{R}_L$ = .54	18	11	9	11	18	11	10	8	11	13	9	11
b = 5.90	5	3	11	8	5	5	11	11	11	8	9	10
n = 192	6	4	24	21	6	20	26	24	26	28	23	17
Own Site			40	44	14	29	41	36	56	58	59	76
Model parameter appear			40	44	36	36	43	49	40	38	35	18
under data set headings			12	4	7	29	7	4	2	4	6	6
in first row			0	8	29	0	5	5	2	0	0	0
			4	0	14	7	1	3	0	0	0	0
			4	0	0	0	3	3	0	0	0	0

[a] AVR - Average Ratio Model

[b] LRS - Linear Regression Slope Model

For the SSI/HIVOL relationship, the receptor models derived from each of the three Philadelphia sites predict the SSI concentrations at all sites in the IP Network outside of Philadelphia with nearly the same accuracy as the model derived from the data taken at those sites. Ninety percent of the SSI concentrations are predicted within ±30% of the true value by the average ratio model derived from the predicted data set while 86%, 92% and 82% of the SSI concentrations at sites outside of Philadelphia are predicted within ±30% by the receptor models derived from 500 S. Broad, Allegheny and St. John's, respectively.

Table 8.3.1 confirms the conclusions drawn from Table 8.2.1 that:

- The average ratio and linear regression slope models predict with approximately equivalent accuracy; hence, the simpler average ratio model is to be preferred.
- Stratification by site type does not enhance the predictive ability of the model.

Concerning site-type classification, the one urban commercial, and two urban industrial site types represented by 500 S. Broad, Allegheny, and St. John's, respectively, predict with approximately equal accuracy. In fact, the average ratio model (.67 average ratio) derived from the urban industrial site at Allegheny is closer to the model (.66 average ratio) derived from the urban commercial data set than is the model (.75 average ratio) yielded by data from the urban commercial site at 500 S. Broad Street. It is interesting to compare the average SSI/HIVOL derived from 60 measurements at urban commercial sites outside of Philadelphia, .66, to the average ratio derived from 194 measurements from all urban commercial sites, .73 (from Table 8.2.1). Apparently the large portion of Philadelphia measurements greatly affects the model parameters.

The final prediction error frequency distributions for average ratio and linear regression slope models show that the model derived from each individual site is a reasonably good predictor for that particular site. Over 96% of the predictions are within ±30% of the measurements.

Table 8.3.2 presents the same analysis for the TOTAL/HIVOL relationship. Here, the number of data pairs available for calculating the ratios is low for all sites except NE Airport (PAPHE) which had 74 simultaneous measurements. None of these models is as good a predictor of TOTAL concentrations at other sites as the SSI/HIVOL models of Table 8.3.1 are, even though they are extremely effective in predicting the TOTAL concentrations at the sites from which they were derived. Approximately 20% of the predicted values in each case differ from the measured values by more than 50%. This is in contrast to only 7% with errors greater than 50% for the TOTAL/HIVOL model derived from all data in Table 8.2.2.

With the exception of the Allegheny model, none of these TOTAL predictors derived from individual Philadelphia sites is as good as the predictor derived from all data, in sharp contrast to the models derived from the SSI/HIVOL relationship in Table 8.3.1 which are just as valid as the model of Equations 8-13 and 8-14.

The SSI/HIVOL average ratios obtained from 500 S. Broad, Allegheny and St. John's differ from the average ratio of Equation 8-13 by +4%, -7% and +8%, respectively while the TOTAL/HIVOL average ratios at 500 S. Broad, Allegheny, NE Airport, Presbyterian Home and St. John's differ from the unstratified ratio of .73 calculated from all data by +8%, -8%, +11%, +11% and +7%, respectively. The higher percent differences are probably due to the lack of HIVOL concentration stratification for the TOTAL/HIVOL model which was found in Table 8.2.2. Because each of the Philadelphia data sets examined in Table 8.3.2 lacked sufficient HIVOL values greater than 100 ug/m^3 which were associated with TOTAL measurements, it was not possible to create such a stratified model from measurements at these sites. The importance of this TOTAL/HIVOL concentration stratification will be addressed shortly. The other reason for this lack of agreement may be the change in HIVOL filter media between 1979 and 1980. The majority of the Philadelphia measurements was taken in 1979 whereas the number of measurements in other areas is greater in 1980 than in 1979. The Philadelphia models may not apply to TOTAL/HIVOL data for this reason. A 1979 and 1980 data stratification might be appropriate to test this.

The relationship between SSI and HIVOL concentrations derived from single sites in a single geographical location is able to produce a model similar to the one derived from many sites and many locations and to predict SSI from HIVOL at geographical locations other than those at which it was derived. Due to the inadequate amount of data available and the possibility of interference due to filter media changes, this conclusion cannot yet be drawn concerning the TOTAL/HIVOL relationship.

Another strategy for forming a receptor model relationship is to locate one set of HIVOL, SSI and/or TOTAL samplers in an area while keeping the existing HIVOL network intact, then using the set of simultaneous measurements from the single site to derive a prediction model for SSI and TOTAL concentrations at the other sites. This possibility is examined for the Philadelphia Bridesburg industrial area (See Figure 4.2.8) using the long-term monitoring site at St. John's to derive the model. The percent error frequency distributions at each site for SSI and TOTAL appear in Table 8.3.3. The distances of these sites from St. John's, as shown in Table 8.3.4, range from .70 (Pilot Freight) to 1.1 km (NE Transfer) with the closest long-term site being Allegheny at a distance of 3.2 km.

The average ratio at St. John's is .78 compared to .67, .61, and .71 at Allegheny (3.2 km distance), Pilot Freight (.70 km distant) and the T & A Pet Shop (2.8 km distance), respectively. SSI data at other sites in the Bridesburg area were insufficient for comparison. Even though these sites are very close together, the average ratio of .72 derived from all sites will be closer to the true model at each site than the one derived from the St. John's data. This is borne out by the SSI/HIVOL prediction error frequency distributions at Allegheny and Pilot Freight where 40% and 39%, respectively, of the predicted values differ from the measured values by more than ±30%. The St. John's model is a good predictor for NE Wastewater, nearly as good as the model derived from that site.

The TOTAL/HIVOL model comparison is more informative since all sites in the Bridesburg area have some TOTAL data with the exception of Allegheny and Pilot Freight. Average ratios at Bridesburg sites range from .75 to .79 and are well represented by the .78 ratio found

TABLE 8.3.3

PREDICTION ERROR FREQUENCY DISTRIBUTIONS
USING MODELS DERIVED FROM ST. JOHN'S TO PREDICT
SSI AND TOTAL CONCENTRATIONS AT OTHER SITES
IN THE BRIDESBURG INDUSTRIAL AREA

	SSI					TOTAL			
	Predicted Data Set Model		St. John's (PAPHI) $\bar{R}_A$ = .78 $\bar{R}_L$ = .84 $\bar{b}$ = 3.50 n = 91			Predicted Data Set Model		St. John's (PAPHI) $\bar{R}_A$ = .78 $\bar{R}_L$ = .70 $\bar{b}$ = 3.50 n = 17	
Predicted Data Set	AVR	LRS	AVR	LRS	Predicted Data Set	AVR	LRS	AVR	LRS
Allegheny	32	39	29	26	Allegheny	14	29	29	36
(PAPHB)	32	31	19	17	(PAPHB)	36	36	21	14
$\bar{R}_A$ = .67	18	19	12	17	$\bar{R}_A$ = .67	7	29	7	7
$\bar{R}_L$ = .50	10	4	18	10	$\bar{R}_L$ = .46	29	0	7	7
b = 16.10	3	1	8	13	b = 17.70	14	7	0	14
n = 77	4	5	14	17	n = 14	0	0	36	21
Pilot Freight	50	50	9	12	Pilot Freight	25	50	8	17
(PAPHJ)	24	24	15	9	(PAPHJ)	25	33	42	42
$\bar{R}_A$ = .61	15	18	38	41	$\bar{R}_A$ = .70	42	8	25	25
$\bar{R}_L$ = .62	9	6	9	3	$\bar{R}_L$ = .53	8	8	8	17
b = .91	0	0	6	15	$\bar{b}$ = 12.80	0	0	17	0
n = 34	3	3	24	21	n = 12	0	0	0	0
NE Wastewater	55	48	52	45	NE Wastewater	54	54	54	46
(PAPHK)	30	36	21	21	(PAPHK)	31	31	31	23
$\bar{R}_A$ = .71	12	12	15	18	$\bar{R}_A$ = .79	0	0	0	23
$\bar{R}_L$ = .78	0	0	6	6	$\bar{R}_L$ = .78	8	8	8	0
b = 4.40	3	0	3	6	$\bar{b}$ = .53	0	0	0	8
n = 33	0	3	3	3	n = 32	8	8	8	0
T&A Pet					T&A Pet	50	50	50	56
(PAPHL)					(PAPHL)	38	41	38	31
	Insufficient Data				$\bar{R}_A$ = .78	9	6	9	9
					$\bar{R}_L$ = .77	3	3	3	0
					b = .92	0	0	0	3
					n = 32	0	0	0	0

TABLE 8.3.3 (Continued)

	SSI					TOTAL			
	Predicted Data Set Model		St. John's (PAPHI)			Predicted Data Set Model		St. John's (PAPHI)	
Predicted Data Set	AVR	LRS	AVR	LRS	Predicted Data Set	AVR	LRS	AVR	LRS
NE Transfer	Insufficient Data				NE Transfer	54	54	54	46
(PAPHM)					(PAPHM)	31	31	31	23
					$\bar{R}_A$ = .75	0	0	0	23
					$\bar{R}_L$ = .71	8	8	8	0
					$\bar{b}$ = 2.40	0	0	0	8
					n = 34	8	6	8	0
Gratz College	Insufficient Data				Gratz College	50	50	50	42
(PAPHN)					(PAPHN)	27	27	23	35
					$\bar{R}_A$ = .77	8	12	15	8
					$\bar{R}_L$ = .80	12	8	8	8
					$\bar{b}$ = .44	4	0	0	4
					n = 26	0	4	4	4
St. John's			55	52	St. John's			59	76
(PAPHI)			31	35	(PAPHI)			35	18
$\bar{R}_A$ = .78			8	8	$\bar{R}_A$ = .78			6	6
$\bar{R}_L$ = .84			2	3	$\bar{R}_L$ = .70			0	0
$\bar{b}$ = 3.50			3	1	$\bar{b}$ = 3.50			0	0
n = 91			1	1	n = 17			0	0

TABLE 8.3.4

PREDICTION ERROR FREQUENCY DISTRIBUTIONS AT PHILADELPHIA SITES USING ST. JOHN'S SSI MEASUREMENTS TO PREDICT SSI CONCENTRATIONS AT OTHER SITES

	Pilot Freight	NE Wastewater	Allegheny	500 South Broad
Distance from St. John's (km)	.44	1.81	3.2	9.4
No. of data pairs	34	35	35	38
Absolute percent difference from prediction using St. John's data.				
0 to 10%	15	24	14	37
10% to 20%	18	32	6	29
20% to 30%	24	24	3	10
30% to 40%	20	9	11	8
40% to 50%	12	3	26	5
50%	12	8	40	10

at St. John's. Eighty to ninety percent of the individual TOTAL concentrations at these sites are predicted to within ±20% by the St. John's model.

In a normal sampling network, a single site, St. John's in the Bridesburg case, would be chosen to represent the entire land use area. Another sampling site meeting the siting criteria which was located several kilometers away in the same area would be just as acceptable. The differences between measurements at these nearby sites reflect the accuracy of using a single sampling site to represent the suspended particulate matter concentrations of an entire area. The differences between mass concentrations at nearby sampling sites in the Bridesburg area was noted in Chapter 5. These differences can be expressed in the same form as the prediction error frequency distributions to compare the measurement accuracy due to sampler siting with the accuracy of the IP prediction models.

In Table 8.3.4, the SSI measurements at St. John's were used to predict the SSI concentrations on the same days at other Philadelphia sites. Unfortunately, only two nearby sites in the Bridesburg area had enough SSI measurements on days simultaneous with those at St. John's to be included. No sites had an adequate number of simultaneous TOTAL measurements to perform a similar analysis for TOTAL concentrations.

The distributions in Table 8.3.4 show that only 57% of the SSI measurements at Pilot Freight, which is less than one kilometer from St. John's, were within ±30% of the St. John's measurements. From Table 8.3.3, the average ratio model predicts 62% of the Pilot Freight values to within ±30%. In this case, the accuracy of the average ratio receptor model is comparable to the accuracy of representing the Pilot Freight SSI concentrations with a nearby, and equally valid, sampling site.

The St. John's average ratio applied to NE Wastewater in Table 8.3.3 predicts more than half of the SSI concentrations at NE Wastewater within ±10% and nearly 90% of the SSI concentrations to within ±30%. This is a substantial improvement over representing the SSI concentrations at NE Wastewater by the simultaneous SSI measurements at nearby St. John's. From Table 8.3.4, only 24% of the NE Wastewater values are estimated to within ±10% by the simultaneous St. John's measurements.

The percent error frequency distributions for Allegheny and 500 S. Broad are included in Table 8.3.4 for comparison purposes even though they are not part of the land use area intended to be sampled by St. John's. The St. John's average ratio model is a better predictor of SSI at Allegheny than are the simultaneous St. John's SSI measurements, though neither one is too accurate; St. John's SSI differs from Allegheny SSI by more than ±30% for more than three-quarters of the simultaneous measurements. The average ratio model predictions differ from measurements by more than ±30% for 43% of the Allegheny measurements.

These data are limited and similar comparisons need to be made in other areas; however, if these relationships between SSI concentrations at nearby sampling sites are representative of the situation in other land use areas and geographical locations, then two conclusions can be drawn:

- The accuracy of the average ratio model for representing IP concentrations is comparable to or better than the accuracy of sampler siting in measuring the overall concentrations in a land use area.
- There is no advantage in deriving an area specific average ratio SSI/HIVOL model over using the average ratio derived from the entire IP Network data set.

Unfortunately, since the TOTAL measurements are so few at closely located sites, similar conclusions cannot be drawn about the TOTAL/HIVOL relationship.

Another approach to defining a model at a specific site which might be more accurate than the average ratio derived from all data is to take simultaneous IP and TSP samples over a period of time, establish the average ratio, and collect only TSP samples thereafter, using the average ratio to estimate IP concentrations. The simultaneous sampling should cover an entire year to contain all probable meteorological and emissions events. None of the sites in the IP Network had collected more than one year of data at the time of this analysis. The ability of one year to represent another year is not yet subject to evaluation. It _is_ possible to divide the SSI/HIVOL and TOTAL/HIVOL data sets from selected sites into two data sets, each containing alternate pairs of values, to calculate the receptor model from one subset, and to test its effectiveness in predicting the SSI or TOTAL measurements from the HIVOL measurements in the other subset.

The prediction error frequency distributions for this procedure applied to SSI/HIVOL and TOTAL/HIVOL measurements at 500 S. Broad, Allegheny, NE Airport, Presbyterian Home, and St. John's sites are presented in Table 8.3.5. The alternate measurement subsets are designated by "odd" and "even", though these designations have nothing to do with the dates on which sampling took place. The model derived from the "odd" set is used to predict the data in the "even" set. Table 8.3.5 also contains the average ratios, slopes and intercepts derived from the "even" sets and the prediction error frequency distributions of the models for each subset predicting their own values, for comparison.

Each of the "odd" models predicts "even" SSI and TOTAL concentrations as well as the models derived from their same data sets. The prediction accuracy is very good for all models with over 80% of the "even" SSI concentrations, with the exception of Allegheny, being estimated to within ±20% by the "odd" models. The TOTAL predictions are nearly as accurate with 100% of the predicted values within ±30% of the measured values.

Thus, it seems that the variability of the size distributions at a specific site is less than the variability of the distributions between sites. If simultaneous IP and TSP data are collected at a site over a period of time, it appears possible to use the model derived from that data to extend the IP data base over adjacent or included periods for which TSP measurements have been taken. This possibility must be evaluated using additional data when they become available.

8.4 Predicting Averages and Maxima of IP from TSP Concentrations

The simplest models derivable from the current IP Network data set for estimating IP concentrations and their precisions from TSP measurements are those of Equations 8-13 and 8-14 for IP measured with the HIVOL size-selective inlet (SSI), and Equations 8-15 to 8-18 for

TABLE 8.3.5

PREDICTION ERROR FREQUENCY DISTRIBUTIONS FOR PHILADELPHIA SITES USING MODELS DERIVED FROM ALTERNATE DATA PAIRS

SSI

Predicted Data Set	Predicted Data Set Model AVR	Predicted Data Set Model LRS	St. John's (PAPHI) (odd) $\bar{R}_A = .75$ $\bar{R}_L = .80$ $\bar{b} = 2.50$ $n = 53$ AVR	St. John's (PAPHI) (odd) $\bar{R}_A = .75$ $\bar{R}_L = .80$ $\bar{b} = 2.50$ $n = 53$ LRS
500 S. Broad	60	58	58	57
(even) (PAPHA)	26	32	28	36
$\bar{R}_A = .75$	9	6	9	4
$\bar{R}_L = .84$	2	0	2	0
$b = 4.70$	0	4	0	2
$n = 53$	2	6	2	2
500 S. Broad			55	51
(odd) (PAPHA)			28	36
$\bar{R}_A = .75$			9	4
$\bar{R}_L = .80$			2	0
$b = 2.50$			0	2
$n = 53$			2	2

TOTAL

Predicted Data Set	Predicted Data Set Model AVR	Predicted Data Set Model LRS	St. John's (PAPHI) (odd) $\bar{R}_A = .78$ $\bar{R}_L = .46$ $\bar{b} = 17.5$ $n = 12$ AVR	St. John's (PAPHI) (odd) $\bar{R}_A = .78$ $\bar{R}_L = .46$ $\bar{b} = 17.5$ $n = 12$ LRS
500 S. Broad	43	50	42	58
(even) (PAPHA)	33	33	25	17
$\bar{R}_A = .81$	17	17	33	17
$\bar{R}_L = .72$	8	0	0	8
$b = 3.80$	0	0	0	0
$n = 12$	0	0	0	0
500 S. Broad			33	33
(odd) (PAPHA)			50	33
$\bar{R}_A = .78$			0	33
$\bar{R}_L = .46$			0	0
$\bar{b} = 17.40$			17	0
$n = 12$			0	0

SSI

Predicted Data Set	Predicted Data Set Model AVR	Predicted Data Set Model LRS	Allegheny (PAPHB) (odd) $\bar{R}_A = .66$ $\bar{R}_L = .49$ $\bar{b} = 15.10$ $n = 38$ AVR	Allegheny (PAPHB) (odd) $\bar{R}_A = .66$ $\bar{R}_L = .49$ $\bar{b} = 15.10$ $n = 38$ LRS
Allegheny	29	32	32	29
(even) (PAPHB)	29	26	26	34
$\bar{R}_A = .68$	18	24	18	24
$\bar{R}_L = .50$	11	11	18	5
$b = 17.40$	11	3	3	3
$n = 38$	3	5	3	5
Allegheny			29	58
(odd) (PAPHB)			42	29
$\bar{R}_A = .66$			18	08
$\bar{R}_L = .49$			5	0
$\bar{b} = 15.10$			0	0
$n = 38$			5	5

TOTAL

Predicted Data Set	Predicted Data Set Model AVR	Predicted Data Set Model LRS	Allegheny (PAPHB) (odd) $\bar{R}_A = .66$ $\bar{R}_L = .50$ $\bar{b} = 14.40$ $n = 7$ AVR	Allegheny (PAPHB) (odd) $\bar{R}_A = .66$ $\bar{R}_L = .50$ $\bar{b} = 14.40$ $n = 7$ LRS
Allegheny	33	33	17	17
(even) (PAPHB)	17	33	50	33
$\bar{R}_A = .62$	33	34	0	50
$\bar{R}_L = .40$	17	0	17	0
$b = 21.00$	0	0	17	0
$n = 6$	0	0	0	0
Allegheny			14	29
(odd) (PAPHB)			29	29
$\bar{R}_A = .66$			29	29
$\bar{R}_L = .50$			14	0
$\bar{b} = 14.40$			14	13
$n = 7$			0	0

TABLE 8.3.5 (Continued)

	SSI					TOTAL			
	Predicted Data Set Model					Predicted Data Set Model		NE Airport (PAPHE) (odd) $\bar{R}_A$ = .81 $\bar{R}_L$ = .79 b = .88 n = 37	
Predicted Data Set	AVR	LRS	AVR	LRS	Predicted Data Set	AVR	LRS	AVR	LRS
NE Airport					NE Airport	43	43	43	43
(PAPHE)					(even) (PAPHE)	48	43	48	48
	Insufficient Data				$\bar{R}_A$ = .82	4	13	9	4
					$\bar{R}_L$ = .92	4	0	0	4
					b = 4.50	0	0	0	0
					n = 23	0	0	0	0
					NE Airport			63	71
					(odd) (PAPHE)			38	29
					$\bar{R}_A$ = .81			0	0
					$\bar{R}_L$ = .79			0	0
					b = .88			0	0
					n = 37			0	0
	Predicted Data Set Model		Pres. Home (odd) (PAPHG)			Predicted Data Set Model		Pres. Home (odd) (PAPHG) $\bar{R}_A$ = .81 $\bar{R}_L$ = .78 b = 1.40 n = 23	
					Pres. Home	43	43	43	43
					(even) (PAPHG)	48	43	48	48
	Insufficient Data				$\bar{R}_A$ = .82	4	13	9	4
					$\bar{R}_L$ = .92	4	0	0	4
					b = 4.50	0	0	0	0
					n = 23	0	0	0	0
					Pres. Home			63	71
					(odd) (PAPHG)			38	29
	Insufficient Data				$\bar{R}_A$ = .81			0	0
					$\bar{R}_L$ = .78			0	0
					b = 1.40			0	0
					n = 23			0	0

TABLE 8.3.5 (Continued)

	SSI					TOTAL			
	Predicted Data Set Model		St. John's (odd) (PAPHI) $\bar{R}_A$ = .80 $\bar{R}_L$ = .84 b = 2.50 n = 48			Predicted Data Set Model		St. John's (odd) (PAPHI) $\bar{R}_A$ = .78 $\bar{R}_L$ = .71 b = 4.00 n = 9	
Predicted Data Set	AVR	LRS	AVR	LRS	Predicted Data Set	AVR	LRS	AVR	LRS
St. John's	47	44	49	49	St. John's	88	100	75	75
(even) (PAPHI)	29	26	26	34	(even) (PAPHI)	13	0	25	25
$\bar{R}_A$ = .76	18	24	18	24	$\bar{R}_A$ = .79	0	0	0	0
$\bar{R}_L$ = .85	11	11	18	5	$\bar{R}_L$ = .66	0	0	0	0
b = 4.40	11	3	3	3	b = 5.00	0	0	0	0
n = 43	3	5	3	5	n = 8	0	0	0	0
St. John's			56	65	St. John's			44	56
(odd) (PAPHI)			26	34	(odd) (PAPHI)			44	44
			18	24	$\bar{R}_A$ = .78			0	0
			18	5	$\bar{R}_L$ = .71			0	0
			3	3	b = 4.00			0	0
			3	5	n = 9			0	0

IP measured by the dichotomous sampler (TOTAL). In the final analysis, the effectiveness of these models can only be judged by their ability to estimate the high 24-hr and annual mean concentrations of IP for comparison against the values of a standard.

To test the effectiveness of the models in making these predictions, sets of measurements from each site were chosen which met one or more of the following requirements:

- The two highest HIVOL concentrations with simultaneous SSI or TOTAL measurements.
- The two highest SSI measurements with simultaneous HIVOL measurements.
- The two highest TOTAL measurements with simultaneous HIVOL measurements.

Some sets of values satisfied more than one of these requirements and in many cases data were insufficient to satisfy all of them. Because of the limited number of simultaneous measurements available, the highest concentrations meeting these criteria at several sites were not "high" by common standards. HIVOL concentrations ranged from 31 to 439 ug/m^3 with the majority in the 100 to 200 ug/m^3 range. Seventy-two pairs of SSI/HIVOL and 144 pairs of TOTAL/HIVOL values met the criteria.

Equations 8-13 and 8-14 were used to predict SSI concentrations and Equations 8-15 to 8-18 were used to predict TOTAL concentrations from HIVOL measurements. The percent error between the predicted and measured concentration was calculated for each SSI/HIVOL and TOTAL/HIVOL pair. The distributions of these errors for SSI and TOTAL appear in Figures 8.4.1 and 8.4.2, respectively. Superimposed on these figures is the Gaussian uncertainty distribution predicted by Equation 8-14 for SSI predictions and Equation 8-18 for the TOTAL predictions.

The first feature to note is that the errors for these high concentrations are not distributed according to a typical normal distribution. In both cases, the distribution seems uniform between -30% and +30%. According to the normal distribution, 68% of the predictions should fall within plus-or-minus one standard deviation

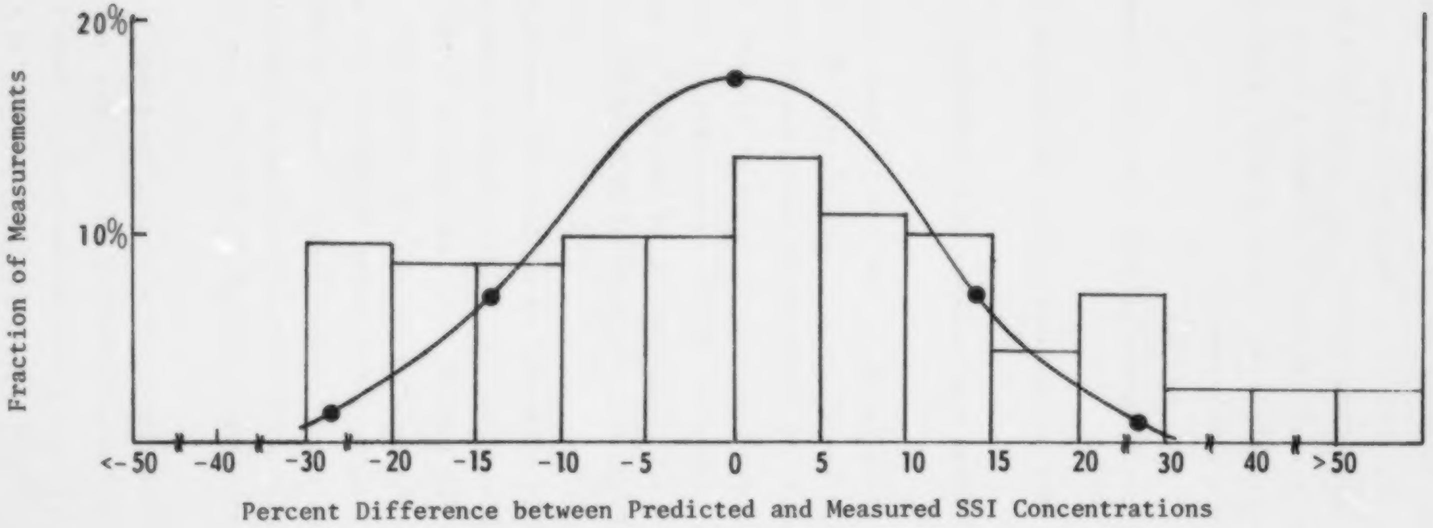

Figure 8.4.1 Histogram of Percent Differences Between Predicted and Measured 24-hr SSI Concentrations for Highest Values at all IP Network Sites. 72 values are included. Dots mark Standard Deviation.

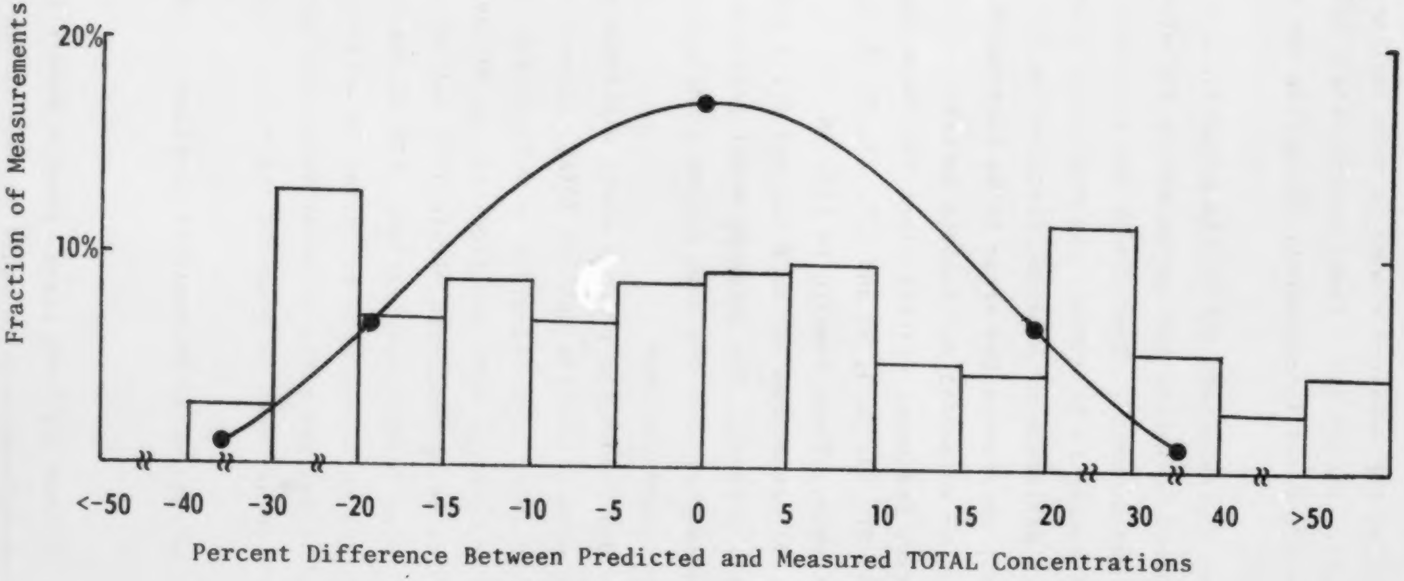

Figure 8.4.2 Histogram of Percent Differences Between Predicted and Measured 24-hr TOTAL Concentrations for Highest Values at all IP Network Sites. 144 values are included. Dots mark Standard Deviation.

and 95% of the predictions should be within two standard deviations (assuming the precision of the measured values is much smaller than this standard deviation). Figure 8.4.1 shows approximately 62% of the predictions within one sigma and approximately 86% within two sigma of measured values for SSI.

Figure 8.4.2 shows approximately 60% of the predictions within plus-or-minus one standard deviation and approximately 93% within ±2 sigma of the TOTAL measurements. Even though the distribution of uncertainties does not appear to be normal, the confidence interval defined by the standard deviation of a normal distribution by Equation 8-10 adequately represents the error to be associated with the high concentrations of suspended particulate matter.

The prediction error frequency distributions for these high concentrations are (44, 31, 12, 3, 3, 3) and (35, 25, 25, 8, 6, 4) for SSI and TOTAL, respectively. These compare to (43, 34, 13, 4, 3, 4) and (32, 25, 22, 8, 5, 7) taken from Tables 8.2.1 and 8.2.2 for the data at all sites in the network. The receptor model predicts individual high concentrations with the same degree of accuracy with which it predicts lower concentrations.

Figures 8.4.3 and 8.4.4 show the percent error distributions of the arithmetic average predictions for SSI and TOTAL, respectively. Only averages containing 20 or more SSI/HIVOL or TOTAL/HIVOL pairs were used. The receptor model is a better predictor of SSI averages, with 100% of the averages being predicted within ±20% and 66% being predicted within ±10%. For TOTAL concentrations, 89% of the averages were predicted within ±20% while 61% were predicted to within ±10% of the measured values. The average ratio receptor model predicts averages with greater accuracy than it predicts individual values.

8.5 Using the IP/TSP Average Ratio to Evaluate Compliance with Standards

If the data used to form and test these receptor models are representative of the measurements which would be made in any part of the United States, then the receptor model of Equation 8-13 is the simplest and most accurate one for predicting IP concentrations

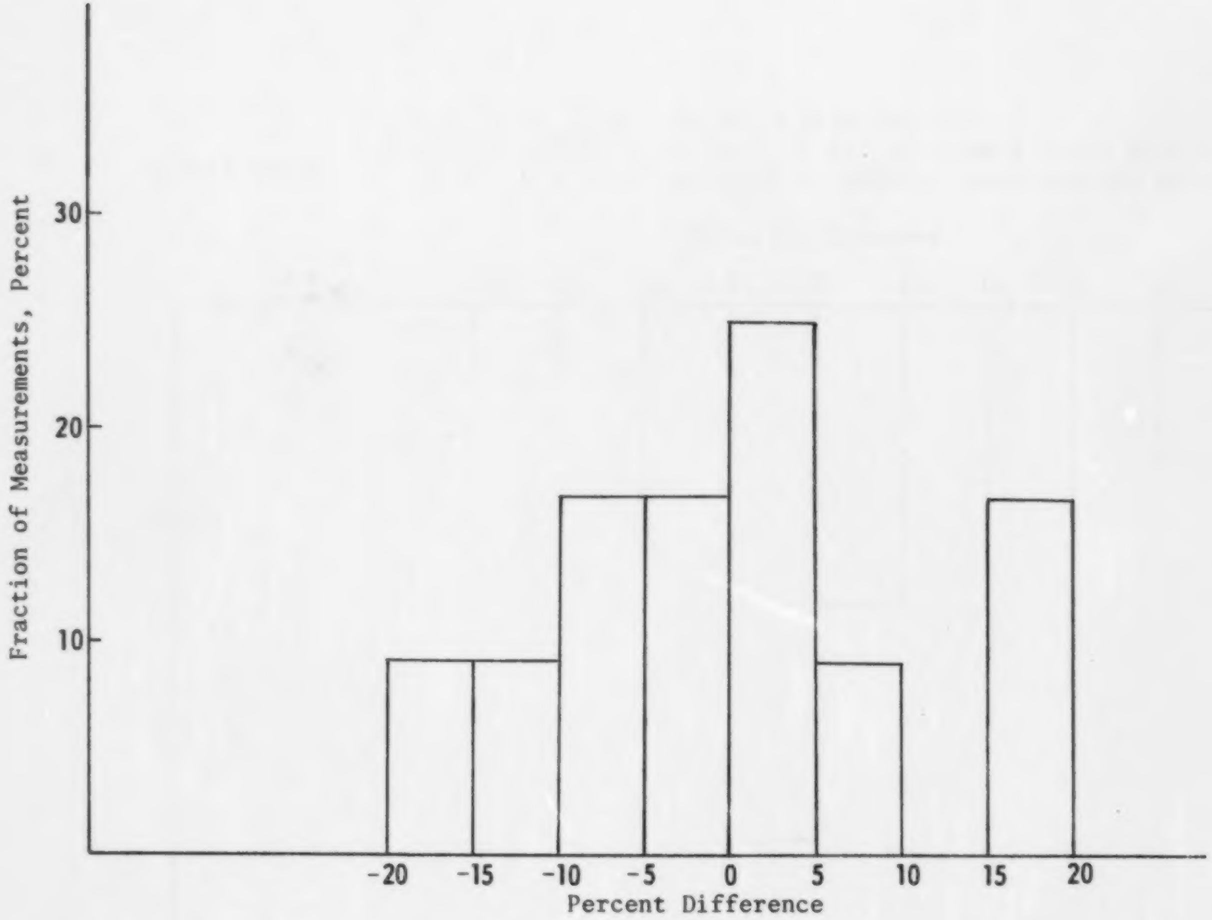

Figure 8.4.3 Histogram of Percent Differences Between Predicted and Measured Arithmetic Averages of SSI at all IP Network Sites with more than 20 data pairs. 12 Values are included.

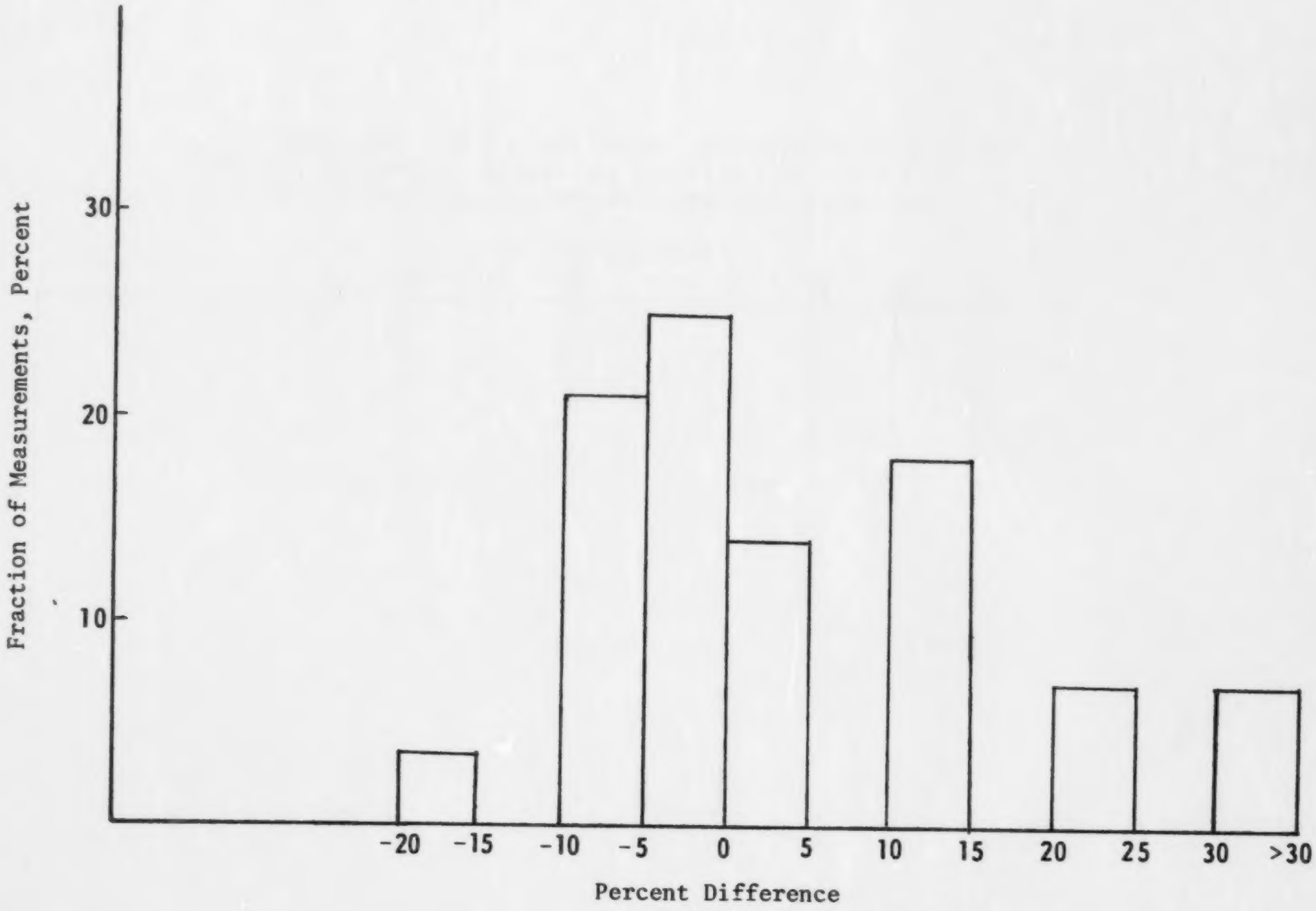

Figure 8.4.4 Histogram of Percent Differences Between Predicted and Measured Arithmetic Averages of Total at all IP Network Sites with more than 20 Data Pairs. 28 values are included.

measured with a size-selective inlet from HIVOL TSP measurements provided the uncertainty expressed by Equation 8-14 is also used to define the confidence interval to be placed around it. Similarly, Equations 8-15 to 8-18 prove to be the simplest and most accurate prediction mechanisms for IP measured by the dichotomous sampler.

Compliance with a 24-hr or arithmetic average determined from these predictions can be looked at in two ways.

First, if the confidence interval around the predicted IP value is comparable to the difference between nearby sampling sites assessing ambient concentrations in the same portion of a neighborhood, as the example of Section 8.3 showed, the argument can be made that the uncertainty of Equation 8-14 is comparable to the sampling precision so that there is no significant difference between the TSP derived IP concentration and one which is actually measured. Therefore, the predicted concentration is as good as a measured one and should be compared against the values of a standard in the same way an ambient measurement is.

A more restrictive, yet safer approach is to add some number of standard deviations to the predicted IP concentration and to compare this value to the standard. If twice the standard deviation derived from Equation 8-14 is added to the prediction of Equation 8-13, and the resulting concentration does not exceed the standard value, then one can be 95% certain that a measurement of IP at that site would not show a violation.

Of course, these estimates should only be used where monitoring data do not exist and decisions based on them should be tempered by the comparisons between predicted and measured IP concentrations made in this chapter. A small but significant portion of the predictions for IP Network data examined here differed by more than 50% from the actual measurements. Without the simultaneous IP and TSP measurements it is imposible to tell which IP prediction will fall into this category.

This chapter has explored the possibility of estimating IP and FP concentrations from TSP concentrations using average ratio and linear regression slope receptor models. The frequency of occurrence of percent differences between predictions based on these models and ambient measurements were used to evaluate the extent to which these models represent reality. Based on the limited data available from the IP Network, the following observations resulted from this analysis:

- No simple relationship between FP and TSP was found which would predict FP from TSP with adequate precision. For IP Network data nearly 70% of the FP predictions differed from the measurments by more than ±20%.
- The average ratio model derived from all IP Network measurements is the simplest relationship between IP and TSP. For SSI and TOTAL IP measurements, stratification by site type does not increase the precision of the model's predictions. The model is independent of TSP concentrations for SSI predictions, but it exhibits a TSP concentration dependency for TOTAL predictions. Seventy-six percent of the SSI measurements and 57% of the TOTAL measurements were predicted to within ±20% by this model in the IP Network.
- Models derived from simultaneous TSP and IP sampling at a single site in an industrial neighborhood predict IP concentrations from TSP concentrations at nearby sites in the neighborhood with a precision which is comparable to the difference in IP measurements obtained from nearby sampling sites.
- Arithmetic average IP concentrations at IP Network sites were predicted from TSP concentrations to within ±20% for all SSI maxima and for 89% of the TOTAL maxima. This degree of uncertainty may be adequate for estimating IP averages for compliance purposes in certain situations.
- Maximum IP concentrations at IP Network sites were predicted from TSP concentrations to within ±20% for 77% of the SSI maxima and for 60% of the TOTAL maxima. The uncertainty associated with predicting maximum concentrations is comparable to that associated with predicting any concentration, irrespective of its magnitude.

CHAPTER 9

IP AND FP COMPOSITION AND SOURCES

The chemical composition of suspended particulate matter has been the subject of a great deal of study in recent years, primarily for two reasons:

- The effects of different chemical species are not equal; some are more harmful than others.
- The composition of suspended particulate matter is indicative of the sources from which it originated.

It is well-known that certain substances, for example lead, cadmium and arsenic, are poisonous at much lower mass concentrations than the tolerable concentrations of calcium or aluminum. The recent National Ambient Air Quality Standard for lead, a 1.5 ug/m^3 quarterly average, was promulgated in recognition of its toxic properties. It is conceivable that other chemically specific standards might be formed in the future. While the toxic nature of certain pollutants measured in the IP Network may be of importance, it is not appropriate to examine this subject here.

Receptor models, which were introduced in Chapter 8, have been devised as a means of using aerosol composition information to estimate the quantities contributed by various emissions sources (Watson et al, 1980). These models have suffered in the past from a lack of sufficient information about the composition of emissions and ambient samples. These needs are slowly being met, and the chemical analyses performed in the IP Network offer a possibility for testing the usefulness of receptor models as a tool for developing national particulate matter emissions control strategies.

In Chapter 4 the potential sources of IP and FP in selected urban areas were identified, their major chemical components were tabulated and their likely particle sizes were noted. Major point source emitters of TSP which had been identified by the National Emissions Data System were located on maps with respect to the sampling sites and speculations were advanced about the relative concentrations of different chemical species in the FINE and COARSE fractions of the ambient samples which would be observed if certain sources were making significant contributions to certain receptors.

This chapter examines the chemical concentration measurements acquired in four of the urban areas described in Chapter 4 to compare the chemical compositions within them and between them and to estimate which sources are the major contributors to FINE and COARSE chemical concentrations. The broader purpose of this examination is not to characterize the source contributions in these urban areas so much as it is to determine the value of routine measurements acquired by the IP Network in attributing ambient concentrations to sources. Chapter 4 took the source-oriented point of view, identifying and locating sources and predicting which aerosol components should be observed at nearby sampling sites if a source were a significant contributor. This chapter looks at the same problem from a receptor-oriented point of view, looking for elevated chemical concentrations that are associated with the emissions of identifiable source types. The approaches are both complementary and reinforcing. Where a receptor-oriented interpretation indicates a source type which is not included in the source-oriented interpretation, such a source must be sought. When the source and receptor-oriented approaches agree, there is strong evidence that the indicated source is affecting the receptor in question.

To evaluate the IP Network data for these purposes, the discussion is broken up into four sections. The first section presents the average and maximum chemical concentrations obtained from EPA validated data summaries for one year at each site in Buffalo, Houston, El Paso, and Philadelphia and examines their external consistency. As noted in Chapter 3, the chemical composition data did not appear to pass through EPA's data validation criteria summarized in Section 3.4, nor were uncertainty estimates available to accompany the data. The data show some inconsistencies among themselves and these are pointed out in Section 9.1.

The second section examines the differences in particle composition as a function of size and location. The central city compositions are compared to the urban scale background site compositions, and similar site types from different urban areas are compared.

In the third section, the chemical element balance receptor model is applied to the average concentrations presented in Section 9.1 to evaluate its usefulness with respect to IP Network data and to estimate source contributions to TOTAL, FINE and COARSE concentrations. The model is also applied to more extensive chemical measurements made on individual samples taken in Philadelphia to determine whether or not additional aerosol measurements would aid source apportionment. The results of optical microscopic analysis of coarse particulate matter from several sites in Philadelphia are also examined in this section.

The final section of this chapter applies the receptor model to average concentrations on a neighborhood scale to study the uncertainties of source attribution which could be due to sampler siting.

9.1 Validity of IP Network Chemical Composition Measurements

Annual average and maximum 24-hr chemical concentrations from the HIVOL, FINE and COARSE samples taken at IP Network sites in Buffalo, Houston, El Paso and Philadelphia are tabulated in Tables 9.1.1, 9.1.2, 9.1.3, and 9.1.4, respectively. Birmingham, Phoenix and Denver are not examined here because these sites lacked sufficient continuous and consistent data at the time of this report. The values in these tables were taken from EPA validated data summaries (EPA, 1981a) and have not been passed through the filter of inequalities 3-1 to 3-4. Before attempting to draw any conclusions from the data, it is helpful to examine their consistency with each other to separate real variability from that variability introduced by the measurement process.

The data validation process through which individual data records pass was insufficient for producing valid summary statistics. The validation procedure did flag inconsistancy of mass measurements; however, flagged data were included in the calculations of averages. The average and maximum concentrations for Big Sister offer a good illustration. Table 9.1.5 presents a series of values which were included in the routine statistical summary supplied by EPA/EMSL.

TABLE 9.1.1

AVERAGE AND MAXIMUM CHEMICAL CONCENTRATIONS IN BUFFALO, NY (10/79 - 9/80)

(Data taken from USEPA, 1981a)

HIVOL CHEMICAL CONCENTRATIONS (ug/m3)

	Sampling Site							
Chemical Species	(1)P.S. No. 26 (NYBUA)		(2)Big Sister(B) (NYBUB)		(3)P.S. No. 28 (NYBUC)		(4)Wilmuth Pump Sta. (NYBUD)	
	Avg	Max	Avg	Max	Avg	Max	Avg	Max
Mass	89.6	(165.3)	38.8	(84.5)	102.9	(190.6)	128.5	(299.8)
Cr	.0068	(.012)	.0038	(.0089)	.011	(.049)	.0137	(.0540)
Cu	.15	(.48)	.08	(.26)	.21	(.63)	.23	(.60)
Fe	2.39	(7.27)	.24	(.65)	2.61	(8.39)	7.10	(15.8)
Pb	.44	(1.24)	.07	(.20)	.33	(1.0)	.91	(5.65)
Mn	.10	(.24)	a	(a)	.16	(.62)	.32	(.84)
Ni	.017	(.06)	a	(.024)	.006	(.021)	.011	(.045)
Ti	.02	(.05)	a	(.01)	.02	(.04)	.03	(.12)
V	.016	(.033)	a	(a)		(.016)	.010	(.032)
$SO_4^=$	15.3	(38.3)	10.0	(23.6)	15.4	(31.0)	20.8	(35.1)
NO_3^-	3.87	(12.3)	3.10	(10.6)	5.89	(17.9)	6.11	(18.9)
No. of Observations:								
Mass		52		37		58		13
Elements		21		19		11		13
Ions		19		17		11		12

[a]Not detectable

TABLE 9.1.1 BUFFALO, NY (Continued)

FINE CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site							
Chemical Species	(1)P.S. No. 26 (NYBUA) Avg	Max	(2)Big Sister(B) (NYBUB) Avg	Max	(3)P.S. No. 28 (NYBUC) Avg	Max	(4)Wilmuth Pump Sta. (NYBUD) Avg	Max
Mass	33.5	(69.8)	17.1	(47.8)	26.9	(58.1)	21.3	(34.8)
Al	.38	(1.54)	.25	(.42)	.28	(.35)	–	
K	.30	(1.26)	.09	(.18)	.40	(1.08)	–	
Ca	.39	(1.11)	.25	(.41)	.58	(.98)	–	
Mn	.03	(.12)	.01	(.02)	.04	(.14)	–	
Cu	.02	(.10)	.03	(.31)	.02	(.04)	–	
Cl	.28	(1.25)	.07	(.13)	.25	(1.00)	–	
Ni	.01	(.03)	a	(.02)	a	(.02)	–	
Ti	.03	(.23)	.02	(.02)	.02	(.02)	–	
Br	.09	(.29)	.02	(.07)	.06	(.13)	–	
Fe	.63	(1.81)	.13	(.29)	.87	(2.66)	–	
Pb	.42	(.96)	.11	(.21)	.38	(.92)	–	
Si	.44	(.90)	.28	(.69)	.39	(.60)	–	
Zn	.11	(.60)	.04	(.09)	.11	(.37)	–	
S	3.29	(8.38)	2.14	(6.65)	2.51	(6.77)	–	
$SO_4^=$	9.6	(24.1)	5.9	(17.0)	6.9	(17.6)	15.50	(25.10)
NO_3^-	1.79	(9.21)	.53	(1.64)	1.41	(4.74)	–	
No. of Observations:								
Mass	52		42		58		14	
Elements	19		14		9		–	
Ions	19		19		10		2	

[a] Not detectable

TABLE 9.1.1 BUFFALO, NY (Continued)

COARSE CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site							
	(1)P.S. No. 26 (NYBUA)		(2)Big Sister(B) (NYBUB)		(3)P.S. No. 28 (NYBUC)		(4)Wilmuth Pump Sta. (NYBUD)	
Chemical Species	Avg	Max	Avg	Max	Avg	Max	Avg	Max
Mass	29.20	(77.60)	5.59	(17.10)	25.10	(73.40)	15.80	(103.80)
Al	1.61	(6.08)	.70	(3.15)	.83	(1.67)	-	
K	.22	(.50)	.08	(.16)	.16	(.30)	-	
Ca	2.72	(5.88)	.45	(1.08)	2.47	(5.52)	-	
Mn	.05	(.15)	.01	(.01)	.06	(.16)	-	
Cu	.03	(.35)	.05	(.78)	.01	(.03)	-	
Cl	1.02	(4.68)	.07	(.20)	.85	(4.67)	-	
Ni	a	(.02)	a	(.03)	a	(.02)	-	
Ti	.05	(.14)	.02	(.03)	.04	(.11)	-	
Br	.02	(.06)	a	(a)	.01	(.03)	-	
Fe	1.68	(8.62)	.21	(.45)	1.36	(3.89)	-	
Pb	.12	(.31)	.02	(.04)	.07	(.16)	-	
Si	2.36	(5.85)	.78	(1.76)	1.68	(4.62)	-	
Zn	.06	(.13)	.02	(.11)	.03	(.07)	-	
S	1.05	(4.47)	.24	(.74)	.52	(1.09)	-	
$SO_4^{=}$	1.9	(10.8)	.6	(1.1)	.9	(1.9)	.70	(.90)
NO_3^{-}	.93	(2.19)	.34	(.85)	.67	(1.33)	-	
No. of Observations:								
Mass	52		42		58		14	
Elements	19		14		9		-	
Ions	19		19		10		2	

[a] Not detectable

TABLE 9.1.2

AVERAGE AND MAXIMUM CHEMICAL CONCENTRATIONS IN HOUSTON, TX (10/79 - 9/80)

(Data taken from USEPA, 1981a)

HIVOL CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site					
Chemical Species	(1)CAMS 8 (TXHOA)		(2)CAMS 1 (TXHOB)		(3)Seabrook(B) (TXHOC)	
	Avg	Max	Avg	Max	Avg	Max
Mass	49.2	(113.5)	86.0	(157.9)	43.7	(87.4)
Cr	.0077	(.0169)	.0112	(.0029)	.0054	(.0089)
Cu	.28	(.45)	.10	(.16)	.27	(.43)
Fe	.78	(1.67)	2.19	(7.90)	.50	(1.28)
Pb	.30	(.49)	.35	(.69)	.11	(.16)
Mn	a	(.06)	.09	(.25)	a	(.04)
Ni	.011	(.031)	.024	(.109)	a	(.006)
Ti	.01	(.01)	.01	(.02)	0.01	(.02)
V	a	(.014)	a	(.030)	a	(.017)
$SO_4^=$	10.5	(18.5)	8.3	(16.4)	6.7	(10.9)
NO_3^-	1.34	(2.78)	1.72	(5.23)	1.35	(2.71)
No. of Observations:						
Mass	18		23		22	
Elements	5		10		6	
Ions	5		9		6	

[a] Not detectable

TABLE 9.1.2 HOUSTON, TX (Continued)

FINE CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site					
	(1)CAMS 8 (TXHOA)		(2)CAMS 1 (TXHOB)		(3)Seabrook(B) (TXHOC)	
Chemical Species	Avg	Max	Avg	Max	Avg	Max
Mass	17.4	(40.5)	23.7	(48.4)	14.3	(43.1)
Al	.43	(.7)	-		.24	(.35)
K	.12	(.17)	-		.14	(.33)
Ca	.32	(.45)	-		.34	(.72)
Mn	.02	(.02)	-		.01	(.01)
Cu	.03	(.05)	-		.01	(.02)
Cl	.16	(.32)	-		.14	(.54)
Ni	.01	(.02)	-		[a]	[a]
Ti	.02	(.03)	-		[a]	(.02)
Br	.05	(.08)	-		.01	(.02)
Fe	.20	(.39)	-		.08	(.15)
Pb	.32	(.50)	-		.10	(.14)
Si	.27	(.36)	-		.27	(.37)
Zn	.07	(.12)	-		.02	(.03)
S	3.18	(5.28)	-		2.15	(4.37)
$SO_4^=$	9.2	(15.7)	-		6.0	(12.7)
NO_3^-	.41	(.55)	-		.68	(1.67)
No. of Observations:						
Mass	8		38		3	
Elements	4		0		6	
Ions	4		0		6	

[a] Not detectable

TABLE 9.1.2 HOUSTON, TX (Continued)

COARSE CHEMICAL CONCENTRATIONS (ug/m^3)

Chemical Species	Sampling Site (1)CAMS 8 (TXHOA) Avg	Max	(2)CAMS 1 (TXHOB) Avg	Max	(3)Seabrook(B) (TXHOC) Avg	Max
Mass	17.0	(28.2)	8.5	(12.0)	18.3	(37.2)
Al	3.15	(7.69)	-		1.20	(2.14)
K	.17	(.22)	-		.20	(.29)
Ca	1.65	(2.57)	-		2.01	(3.25)
Mn	.02	(.02)	-		.01	(.02)
Cu	.02	(.03)	-		.10	(.51)
Cl	1.11	(2.95)	-		.70	(1.99)
Ni	.01	(.02)	-		a	(a)
Ti	.02	(.04)	-		.03	(.05)
Br	.02	(.03)	-		a	(a)
Fe	.61	(.96)	-		.32	(.64)
Pb	.08	(.12)	-		.03	(.04)
Si	1.79	(3.37)	-		2.30	(4.02)
Zn	.04	(.07)	-		.02	(.07)
S	1.01	(2.45)	-		.49	(1.65)
$SO_4^=$	2.1	(4.6)	-		1.1	(2.7)
NO_3^-	1.15	(1.68)	-		1.33	(2.00)
No. of Observations:						
Mass	8		38		3	
Elements	4		-		6	
Ions	4		-		6	

[a] Not detectable

TABLE 9.1.3
AVERAGE AND MAXIMUM CHEMICAL CONCENTRATIONS IN EL PASO, TX (10/79 - 9/80)
(Data taken from USEPA, 1981a)

HIVOL CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site			
	(1)El Paso (TXELA)		(2)Clint(B) (TXELB)	
Chemical Species	Avg	Max	Avg	Max
Mass	115.2	(319.8)	86.7	(240.2)
Cr	.0047	(.0089)	.0042	(.0089)
Cu	.37	.80)	.46	(1.37)
Fe	1.60	(2.44)	1.05	(2.67)
Pb	1.16	(2.27)	.18	(.59)
Mn	.07	(.15)	a	(.09)
Ni	a	(.006)	a	(.0006)
Ti	.02	(.03)	.02	(.06)
V	a	(.015)	a	(a)
$SO_4^=$	5.7	(8.4)	4.3	(8.5)
NO_3^-	1.69	(3.04)	1.13	(2.59)

No. of Observations:

Mass	43	40
Elements	9	40
Ions	9	16

[a] Not detectable

TABLE 9.1.3 EL PASO, TX (Continued)

FINE CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site			
Chemical Species	(1)El Paso (TXELA) Avg	Max	(2)Clint(B) (TXELB) Avg	Max
Mass	23.0	(137.3)	12.3	(28.9)
Al	.41	(.60)	.32	(.53)
K	.23	(.50)	.16	(.45)
Ca	.83	(1.21)	.48	(.76)
Mn	.01	(.02)	.01	(.01)
Cu	.05	(.10)	.02	(.04)
Cl	.43	(1.63)	.08	(.20)
Ni	a	(a)	a	(a)
Ti	.02	(.02)	.02	(.02)
Br	.16	(.43)	.03	(.11)
Fe	.17	(.33)	.12	(.28)
Pb	.74	(1.59)	.15	(.45)
Si	.52	(.73)	.50	(1.50)
Zn	.14	(.35)	.03	(.12)
S	.94	(1.65)	.96	(3.43)
$SO_4^=$	2.3	(4.1)	2.6	(9.2)
NO_3^-	.47	(2.18)	.54	(1.55)
No. of Observations:				
Mass	27		38	
Elements	6		15	
Ions	7		16	

[a] Not detectable

TABLE 9.1.3 EL PASO, TX (Continued)

COARSE CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site			
Chemical Species	(1)El Paso (TXELA) Avg	Max	(2)Clint(B) (TXELB) Avg	Max
Mass	46.6	(151.7)	45.8	(141.8)
Al	1.87	(3.82)	2.01	(3.69)
K	.50	(.92)	.53	(1.07)
Ca	6.05	(14.12)	2.86	(5.59)
Mn	.04	(.08)	.02	(.03)
Cu	.07	(.12)	.03	(.11)
Cl	.24	(.54)	.20	(.38)
Ni	a	(a)	a	(a)
Ti	.07	(.14)	.05	(.13)
Br	.04	(0.12)	a	(.02)
Fe	.92	(1.74)	.67	(1.27)
Pb	.21	(.54)	.05	(.15)
Si	5.24	(9.79)	4.93	(10.33)
Zn	.07	(.18)	.02	(.04)
S	.33	(.52)	.28	(.72)
$SO_4^=$	.7	(1.4)	.8	(1.5)
NO_3^-	.47	(1.17)	.45	(.87)
No. of Observations:				
Mass	27		38	
Elements	6		15	
Ions	7		16	

[a] Not detectable

TABLE 9.1.4
AVERAGE AND MAXIMUM CHEMICAL CONCENTRATIONS IN PHILADELPHIA (10/79 - 9/81)
(Data taken from USEPA, 1981d)

HIVOL CHEMICAL CONCENTRATIONS (ug/m^3)

Chemical Species	Sampling Site (14)500 S. Broad (PAPHA) Avg	Max	(1)Allegheny (PAPHB) Avg	Max	(2)St. John's (PAPHI) Avg	Max	(11)Presbyterian Home (PAPHG) Avg	Max	(10)NE Airport (B) (PAPHE) Avg	Max
Mass	65.5	(179.4)	119.7	(439.4)	68.0	(200.1)	58.0	(161.5)	48.3	(137.1)
Cr	.0062	(.0187)	.0142	(.0368)	.0080	(.0227)	0.0060	(0.0130)	0.0059	(0.0089)
Cu	.17	(.43)	.33	(1.49)	.32	(1.36)	0.11	(0.31)	0.10	(0.20)
Fe	1.04	(3.52)	4.27	(12.56)	1.48	(5.69)	0.76	(2.31)	0.74	(2.43)
Pb	.56	(2.97)	.85	(2.43)	.89	(2.60)	0.53	(2.54)	0.47	(1.55)
Mn	a	(.35)	.37	(1.79)	.06	(.39)	a	(0.08)	a	(0.22)
Ni	.024	(.162)	.029	(.134)	.024	(.138)	0.012	(0.038)	0.017	(0.117)
Ti	.02	(.13)	.04	(.09)	.02	(.11)	0.01	(0.05)	0.01	(0.04)
V	.036	(.214)	.045	(.192)	.037	(.192)	0.022	(0.070)	0.025	(0.127)
$SO_4^=$	12.8	(48.6)	12.2	(60.0)	10.6	(38.0)	13.6	(32.3)	10.4	(24.9)
NO_3^-	3.17	(16.46)	3.06	(14.26)	2.36	(14.30)	3.70	(9.12)	2.53	(11.40)
No. of Observations:										
Mass	116		97		106		103		99	
Elements	98		51		54		19		26	
Ions	98		53		47		18		24	

[a]Not detectable

TABLE 9.1.4 PHILADELPHIA, PA (Continued)

FINE CHEMICAL CONCENTRATIONS (ug/m^3)

Chemical Species	Sampling Site (14)500 S. Broad (PAPHA) Avg	Max	(1)Allegheny (PAPHB) Avg	Max	(2)St. John's (PAPHI) Avg	Max	(11)Presbyterian Home PAPHG Avg	Max	(10)NE Airport (B) PAPHE Avg	Max
Mass	23.5	(69.3)	24.3	(82.1)	30.1	(100.6)	30.9	(127.5)	23.10	(99.3)
Al	.30	(.46)	-		-		.33	(.68)	.26	(.04)
K	.18	(.46)	-		-		.15	(.55)	.13	(.23)
Ca	.16	(.38)	-		-		.26	(.38)	.21	(.32)
Mn	.02	(.03)	-		-		.02	(.05)	.01	(.02)
Cu	.06	(.15)	-		-		.02	(.06)	.02	(.04)
Cl	.12	(.25)	-		-		.18	(.46)	.10	(.50)
Ni	.03	(.05)	-		-		.02	(.10)	.01	(.03)
Ti	.03	(.06)	-		-		.03	(.11)	.02	(.03)
Br	.12	(.30)	-		-		.15	(.51)	.10	(.33)
Fe	.24	(.43)	-		-		.21	(.82)	.12	(.26)
Pb	.73	(1.46)	-		-		.64	(2.31)	.39	(1.31)
Si	1.41	(2.40)	-		-		.28	(.98)	.26	(1.13)
Zn	.25	(.94)	-		-		.15	(.75)	.08	(.25)
S	4.16	(5.57)	-		-		3.22	(13.14)	2.52	(5.65)
$SO_4^=$	-		-		-		10.4	(35.9)	6.5	(16.20)
NO_3^-	-		-		-		.63	(2.61)	.5	(3.42)
No. of Observations:										
Mass	39		22		14		60		112	
Elements	5		0		0		17		23	
Ions	0		0		0		19		26	

TABLE 9.1.4 PHILADELPHIA, PA (Continued)

COARSE CHEMICAL CONCENTRATIONS (ug/m^3)

Chemical Species	Sampling Site (14)500 S. Broad (PAPHA) Avg	Max	(1)Allegheny (PAPHB) Avg	Max	(2)St. John's (PAPHI) Avg	Max	(11)Presbyterian Home (PAPHG) Avg	Max	(10)NE Airport (B) (PAPHE) Avg	Max
Mass	18.9	(47.2)	35.3	(89.8)	18.1	(48.8)	16.9	(34.1)	13.5	(43.7)
Al	1.81	(2.84)	-		-		.97	(2.88)	.81	(1.82)
K	.41	(.64)	-		-		.19	(.46)	.15	(.40)
Ca	1.50	(3.24)	-		-		.84	(1.68)	.53	(1.17)
Mn	.03	(.05)	-		-		.02	(.04)	.01	(.03)
Cu	.03	(.07)	-		-		.01	(.03)	.01	(.02)
Cl	.41	(.86)	-		-		.21	(.83)	.31	(2.34)
Ni	.01	(.03)	-		-		a	(.05)	a	(.02)
Ti	.13	(.18)	-		-		.05	(.18)	.04	(.12)
Br	.05	(.08)	-		-		.04	(.14)	.02	(.08)
Fe	1.29	(2.03)	-		-		.71	(2.45)	.47	(1.49)
Pb	.20	(.37)	-		-		.16	(.47)	.10	(.28)
Si	5.52	(9.84)	-		-		1.96	(5.36)	1.38	(4.18)
Zn	.15	(.48)	-		-		.08	(.43)	.04	(.15)
S	.93	(1.51)	-		-		.49	(1.87)	.29	(1.64)
$SO_4^=$	-		-		-		1.1	(3.50)	.8	(2.9)
NO_3^-	-		-		-		.75	(2.51)	.67	(2.65)
No. of Observations:										
Mass	39		22		14		60		112	
Elements	5		0		0		17		23	
Ions	0		0		0		19		26	

[a] Not detectable

TABLE 9.1.5

EXAMPLES OF INCONSISTENT OBSERVATIONS AT ANGOLA BIG SISTER (NYBUB), NY (10/79 - 9/80)

(Data from USEPA, 1981a)

Date	HIVOL Mass ug/m^3	COARSE Mass ug/m^3	Al in COARSE ug/m^3	FINE Mass ug/m^3	Al in FINE ug/m^3
10/18/79	48.4	9.4	-	41.7	-
02/09/80	24.4	15.5	-	16.8	-
02/15/80	14.4	2.8	-	15.6	-
02/21/80	25.0	5.0	.39	21.7	.23
08/07/80	60.0	80.0	44.39	49.50	4.22
08/13/80	34.2	63.7	-	16.6	-
08/19/80	49.2	134.7	-	34.6	-
08/25/80	47.0	100.8	-	35.7	-
08/31/80	59.0	75.0	26.67	38.0	2.02
09/06/80	49.7	77.7	-	26.1	-
09/12/80	56.8	119.3	-	139.0	-
09/18/80	28.3	26.7	-	10.3	-
09/30/80	52.2	75.7	-	35.4	-
Orig. Avg. (Maximum)	39.7 (84.5)	18.6 (134.7)	4.78 (44.6)	21.8 (139.0)	.59 (4.22)
No. of Observations	50	55	17	55	17
Corrected Avg. (Maximum)	38.8 (84.5)	5.59 (17.1)	.70 (3.15)	17.10 (47.8)	.25 (.42)
No. of Observations	37	42	14	42	14

These thirteen sampling days were singled out because they are internally inconsistent; the TOTAL concentrations are greater than the HIVOL concentrations, in many cases (8/7/80, 8/13/80, 8/19/80, 8/25/80, 8/31/80, 9/6/80, 9/12/80, 9/30/80) by over a factor of two. The aluminum concentrations measured on 8/7/80 and 8/31/80 are unreasonable for a rural site such as Big Sister (they are unreasonable at any site). The effect of removing these 13 records on the average and maximum concentrations is seen in the final rows of Table 9.1.5. Though the HIVOL average and maximum do not change by much, the COARSE mass and aluminum average and maximum drop precipitously and the FINE mass average and maximum are considerably different. The averages and maxima for Big Sister which are reported in Table 9.1.1 are the averages of the data set without the 13 records of Table 9.1.5.

Other internally inconsistent records were observed in the data sets from which the statistics in Tables 9.1.1, 9.1.2, 9.1.3 and 9.1.4 were derived, but they were not as extreme as those evidenced in Table 9.1.5 and corrections were not made. Significant biases in these summaries could exist, however, and some additional data validation criteria to remove grossly inconsistant values need to be applied to mass and chemical data acquired by the IP Network before statistical summaries are produced. Summaries should not be produced or used without a prior examination of the individually flagged data records.

Most of the individual chemical concentration measurements from which the averages were derived were made on the same days, so there should be consistency between HIVOL and TOTAL (sum of FINE and COARSE) measurements. HIVOL measurements, eg. Mass, Fe, Pb, Mn, Ni, $SO_4^=$ and NO_3^-, should be greater than or equal to TOTAL measurements of the same species. For those species which are known to be concentrated in the fine particles, Pb, Ni, $SO_4^=$ and NO_3^-, HIVOL concentrations should not exceed TOTAL concentrations by a large amount.

For Mn, Ti and Ni, many measurements are at or near their detection limits, so the sum of FINE and COARSE concentrations of these elements and the HIVOL concentrations will experience large uncertainties. The HIVOL and TOTAL concentrations are normally within factors of 2 or 3 of each other, which is to be expected.

The possibility of a bias to Cu concentrations due to the HIVOL exhaust was raised in Chapter 3. This would cause HIVOL and SSI Cu concentrations to be higher than TOTAL concentrations. This is borne out by the Cu measurements. Average HIVOL Cu concentrations are factors of 2 to 5 times higher than corresponding average TOTAL Cu concentrations at most sites. At Clint, Texas, this approaches a factor of 9, but because the TOTAL Cu concentration is so close to the lower quantifiable limit there is a large uncertainty associated with its measurement. These discrepancies indicate that some of the HIVOL exhaust may be recirculated through the sampler.

Pb and Fe average concentrations on HIVOL and TOTAL samples generally agree with each other. In a few cases, notably Big Sister in Buffalo and 500 S. Broad in Philadelphia, the HIVOL Fe and Pb average concentrations equal approximately 60% of the corresponding TOTAL concentrations. These averages come from different sample sets, however, (only 5 samples are contained in the TOTAL averages while the HIVOL averages used 98 samples at 500 S. Broad) so the difference is probably not due to biases in the measurement process.

The sulfate and nitrate concentrations on HIVOL and SSI samples were shown to possess a possible bias due to adsorption of sulfur dioxide and nitrogen dioxide gases by the filter medium. The comparison of HIVOL and TOTAL average sulfate and nitrate concentrations in the four cities bears this out. Presumably most of the variability between HIVOL and TOTAL sulfate and nitrate concentrations is due to samples taken in 1980. The average HIVOL sulfate is normally 1.5 to 2 times higher than the TOTAL average and the average HIVOL nitrate is 2 to 3 times higher than corresponding TOTAL averages. These results are consistent with the artifact hypothesis.

On FINE and COARSE samples, sulfur was measured by x-ray fluorescence and sulfate was measured by automated colorimetry. If most of the sulfur is in the form of sulfate, then the sulfate concentrations should equal approximately three times the sulfur concentrations. For all FINE samples the $SO_4^=/S$ concentration ratio varies from 2.5 to 3.2. Since the average S and $SO_4^=$ concentrations were not necessarily derived from analyses on the same set of samples, this agreement is reasonable and lends credibility to both the XRF and colorimetric measurement methods. Several of the COARSE $SO_4^=$/S ratios are closer to 2, notably those at NYBUA, NYBUB, TXHOA, TXHOC, and TXELA. This could be due to sulfur in the COARSE particles which is not in the form of sulfate, and given the good agreement between analytical methods for the FINE sulfate and sulfur averages, there is no reason to suspect a measurement difficulty.

The Cr and V concentrations measured on the HIVOL samples place an upper limit on what should be expected on the FINE and COARSE samples. X-ray fluorescence is perfectly capable of measuring Cr and V on the FINE and COARSE samples at no additional analysis cost, but these concentrations are not included in the IP Network data summaries. They should be reported for intercomparison with the corresponding HIVOL concentrations and because, as Table 4.2.1 shows, Cr and V are important constituents of steel making and residual oil combustion emissions, respectively.

This check of external consistency is by no means a substitute for sample by sample validation and flagging of individual measurements. These can only be done as part of the normal validation procedure, however, and cannot be attempted here. In general, the average chemical concentrations of HIVOL, COARSE and FINE samples from the urban areas under study are within the ranges to be expected from such samples. They should be used with the following caveats:

- Ti, Mn, Ni and Cu concentrations are often at or near their lower quantifiable limits (approximately .01 ug/m^3) where their uncertainties will be large.
- Cu concentrations on HIVOL samples may be positively biased due to exhaust recirculation.
- HIVOL sulfate and nitrate values may be positively biased due to the adsorption of sulfur and nitrogen containing gases by the filter medium. This is probably more prevalent for samples taken in 1980.

With these observations about the validity of IP Network chemical composition data in mind, it is possible to study the relationships between sources and receptors in some representative urban areas.

9.2 Urban-Scale Chemical Compositions and Possible Source Types

Three comparisons of the average chemical concentrations presented in Tables 6.1.1 to 6.1.4 are important to gain an understanding of the chemical character and possible sources of the IP concentrations in urban areas:

- Comparison of the chemical compositions of the FP and CP size fractions.
- Comparison of the FP and CP chemical concentrations at urban sites with those at the urban-scale background site.
- Comparison of typical urban concentrations in one city to those in another city.

In the process of making these comparisons, reference will be made to the maps locating sampling sites with respect to sources in Chapter 4, to the speculations advanced there about which chemical concentrations might be elevated by contributions from nearby sources, and to Table 4.2.1 which relates the particle size and chemical composition of the aerosol to sources types in each urban area. In this way differences between chemical concentrations for different size ranges, sampling locations and cities can be related to differences in the size, location and city of source emissions.

With regard to particle size, all sites in all of the cities studied show the Al, Si, Fe and Ca concentrations to be significantly greater in the CP fraction. Similarly, the Pb, Br, S, $SO_4^=$, concentrations are highest in the FP fraction. Referring to the dominant particle size and chemical concentration columns of Table 4.2.1 shows that the CP species are common to geological material while the FP Pb and Br are associated with leaded auto exhaust. Chlorine concentrations are highest in the CP fractions in Buffalo, Houston and Philadelphia. The exception is in El Paso, TX where the average FP Cl is nearly twice the CP Cl. CP Cl could result from sea salt or the salting of roads in the winter. The FP Cl, as Table 4.2.1 shows, might be associated with vegetative burning. Average snowfall in Houston (Table B.1 of Appendix B) is only .4 inches/year, so road salting is improbable there, but it is close enough to the Gulf of Mexico to receive a marine influence. Buffalo is too distant from the ocean for sea salt to be a large contributor to CP Cl, but its snowfall is sufficient to require extensive salting of roads. Philadelphia's CP Cl could receive influences from both source types. In El Paso, neither the marine nor salting (annual snowfall is only 4.7 inches) would be major contributions to CP Cl, but the large quantity of wood, trash and brush burning in neighboring Juarez could contribute Cl to the FP fraction.

The FP and CP fractions of Cu, Mn, Ni, Ti, and K concentrations tend to be equal at most sites. As noted in the previous section, Cu, Mn, Ni and Ti concentrations are often at or near the detection limit, which is consistent with this equality. Nitrate and zinc concentrations tend to be nearly equally distributed between the FP and CP fractions or in the FP fraction, depending on the site.

With respect to comparisons between sampling sites within each urban area, chemical concentrations in both FP and CP fractions at urban sites often show enrichments over corresponding concentrations at the urban-scale background sites. Thus, local sources are likely contributors to most of the chemical species measured.

In Buffalo, NY, the two urban sites show average FP chemical concentrations which are nearly equal to each other. The Al, Si, K, Fe and Cl concentrations at P.S. 26 are 1.5 to 2 times higher than they are at P.S. 28. Reference to the site survey summaries in Table 3.1.3 shows that moderately traveled roads are closer to P.S. 26 then they are to P.S. 28. Higher FP and CP Pb and Br levels at P.S. 26 might be due to more auto exhaust from cars on these roads. The elevated CP Cl suggests resuspended road dust with salt in it. Both FP and CP Fe concentrations at these sites are 5 to 8 times higher than background, consistent with the proximity to steel mills noted in Chapter 4. FP and CP sulfate and nitrate at P.S. 26 are also higher than those at P.S. 28 with no obvious explanation. Because vanadium data are unavailable and Ni concentrations are so close to detection limits, the effects of residual oil combustion proposed in Chapter 4 cannot be discerned from these data.

In the Houston urban area there is some enrichment with respect to the urban-scale background site for most FP chemical concentrations at CAMS8; Al, Fe, Zn, Pb, Br and sulfate show elevated levels. In the

CP fraction Al, Cl, Fe, Pb and sulfate are higher at the site closer to the city. Oddly, several concentrations, Si, Ca and Cu, are higher at the background site. The number of samples from which these averages were calculated is small for both sites, so they may not be representative. At CAMS8, the CP Al concentration is nearly double the Si concentration, which is unusual for the geologically dominated CP fraction. The maximum Al concentration, 7.7 ug/m^3, is higher than the maximum at any other site, and because only four samples were included in the average, it raises the average substantially. This is another example of the need for validation of individual data items prior to the calculation of averages. The elevated Fe levels may be due, in part, to the nearby steel foundry, while the Pb and Br are most likely contributed by automobile traffic along the ship channel.

In El Paso, Pb and Br are elevated at the urban site, most likely due to auto exhaust, though a portion of the Pb may be due to the smelter. Ca, Cu, Cl, and Zn are also elevated in the FP fraction. The Cl, as noted earlier, may result from vegetative burning while the Zn and Cu may come from the smelter. In the CP fraction the Ca average is very high, but the small number of samples gives the high maximum concentration, 14.1 ug/m^3, more weight than it deserves; this appears to be another example of the need for data validation. Pb and Zn are higher, possibly due to the smelter, but most other urban CP concentrations are similar to those at the background site. Of the four cities studied here, El Paso is the least industrialized and the comparison between urban and background chemical concentrations reflects that.

In Philadelphia, both the NE Airport and Presbyterian Home sites are in residential areas; they are not true background sites. FP Pb and Si are high at 500 S. Broad with respect to the other sites. Pb, and the associated Br, once again are probably due to auto exhaust. The FP Si maximum of 2.4 ug/m^3 is much higher than the maxima at other sites and in other cities; this biases the average. In the CP fraction Al, Si, and Ca are elevated at 500 S. Broad with respect to the other sites. Resuspended dust from traffic is consistent with the site survey summary in Table 3.1.3 and with the elevated Pb and Br in the FP fraction. Reference to Figure 4.2.7 shows no major industrial sources close to any of the sites and this is consistent with the uniform average concentrations among the three sites.

With regard to comparisons between cities, several differences can be noted. It is helpful to perform this comparison with respect to a fixed reference as well as among the cities included in this study. Tables 6.2.1 and 6.2.2 have been compiled for this purpose. Table 6.2.1 lists averages of the average chemical concentrations at IP Network sites reporting over 5 measurements. These averages are classified by site type and size fraction. Table 6.2.2 presents the highest average found at any one of the sites listed in the last row of Table 6.2.1. Observations similar to those which have been made for the individual cities apply to the figures in these tables. Automotive-related elements and sulfate are in the FP fractions while geologically related elements, Al, Si, Ca, Ti, and Fe tend to be higher in the CP fraction. With the exception of the rural classification, where all concentrations are lower, the CP and FP average concentrations are relatively constant for all site types. This is to be expected since the site-type classifications do not consider specific sources affecting individual sites; these sources can vary considerably for different sites even though the site types may be the same.

The FP chemical concentrations at the urban sites in the four cities are generally similar to those of urban and suburban sites in Table 9.2.1 and generally less than the extreme values of Table 9.2.2, except where individual high values at a site bias the average, as has been previously noted. FP Fe is higher than the other cities in Buffalo, which is consistent with the large steel industry there, and FP Pb in El Paso is elevated with respect to Table 9.2.1 and other cities, which might be due to the smelter. FP sulfate concentrations in El Paso are significantly less than those in Table 9.2.1 and the other cities, which is consistent with the regional-scale nature of this aerosol component. El Paso receives virtually no transported pollutants whereas the other cities are subject to regional-scale sulfate.

TABLE 9.2.1

ARITHMETIC AVERAGE CHEMICAL CONCENTRATIONS STRATIFIED BY SITE TYPE

Concentrations in ug/m3, these concentrations are averages of the averages at the indicated sites

Site Type:	Urban-Industrial			Urban-Non-industrial			Suburban-Industrial			Suburban-Non-industrial			Rural		
Size Fraction: Chemical Species	TSP	FP	CP	TSP	FP	CP	TSP	FP	CP	TSP	FP	CP	TSP	FP	CP
Mass	96.49	26.96	24.52	73.73	25.44	22.96	112.65	30.30	27.10	74.95	21.51	19.53	51.12	12.88	20.90
Al	-	.32	1.06	-	.38	1.21	-	.47	1.53	-	.39	1.05	-	.52	1.11
Si	-	.47	2.17	-	.38	2.80	-	.67	3.22	-	.49	2.49	-	.50	2.00
S	-	2.80	.55	-	1.93	.32	-	2.75	.35	-	1.42	.30	-	1.30	.26
Cl	-	.19	.37	-	.22	.60	-	.15	.12	-	.22	.71	-	.09	.24
K	-	.30	.19	-	.17	.24	-	.17	.21	-	.14	.24	-	.15	.20
Ca	-	.58	2.24	-	.36	1.64	-	.68	3.39	-	.36	1.23	-	.42	1.10
Ti	-	.02	.04	-	.02	.05	-	.02	.05	-	.02	.05	-	.02	.03
V	.01	-	-	.01	-	-	a	-	-	a	-	-	a	-	-
Cr	.01	-	-	.01	-	-	.01	-	-	.01	-	-	.01	-	-
Mn	.14	.02	.03	.03	.02	.02	.08	.03	.02	.03	.01	.02	a	.01	.01
Fe	2.77	.50	1.09	1.22	.18	.72	1.81	.34	.72	1.27	.13	.60	0.66	.15	.31
Ni	.01	a	a	.01	.01	a	a	a	a	.01	a	a	a	a	a
Cu	.23	.02	.01	.26	.02	.02	.43	.05	.09	.34	.03	.02	.31	.02	.03
Zn	-	.08	.03	-	.08	.04	-	.22	.09	-	.06	.03	-	.02	.01
Br	-	.07	.01	a	.10	.03	-	.11	.03	-	.11	.02	-	.02	a
Sn	-	.05	.04	-	.05	.04	-	.095	.04	-	.04	.04	-	.05	.04
Pb	.54	.34	.08	.45	.41	.11	.44	.49	.11	.52	.42	.10	.09	.10	.03
$SO_4^=$	12.10	7.95	1.05	9.79	5.61	1.15	10.95	8.20	.70	7.85	4.92	.83	5.74	3.60	.80
NO_3^-	4.04	1.18	.95	3.09	.71	.74	1.73	.52	.68	4.75	1.27	1.05	1.70	1.29	.56
Sampling Sites Included in Averages:	KSKAA, NYBUA, NYBUC, NYBUD[b,c] OHAKA, PAPHB[b,c] PAPHI[b,c], TXHOB[b,c]			ALBIA, CASJA, CODEA[b,c], CTHFA, DEDOA, MABOA, MABOB, MNMIA, MNMIB, MOSLA, MOKAA, ORPOB, PAPHA[b,c], PAPHG, OHCLA, OHSTA[b,c] TXDAA, TXELA			ALBIC[b,c], ALBIE			ALBIB, ALBID AZPHC, CALAA[b,c], CALAB, CASFA, CASFB, MIHOA[b,c] PAPHE, WASEB			AZPHA, CAFPA, ILBRA, MEACA[b,c], ORPOA, TXELB, TXHOC,		

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[a] Not detectable.

[b] Sampling sites do not have elemental data for FP & CP.

[c] Sampling sites do not have ion data for FP & CP.

TABLE 9.2.2

HIGHEST AVERAGE CHEMICAL CONCENTRATIONS STRATIFIED BY SITE TYPE

Concentrations in ug/m^3, these concentrations are the highest average from any one of the sites listed in Table 9.2.1

Site Type:	Urban-Industrial			Urban-Non-industrial			Suburban-Industrial			Suburban-Non-industrial			Rural		
Size Fractions: Chemical Species	TSP	FP	CP	TSP	FP	CP	TSP	FP	CP	TSP	FP	CP	TSP	FP	CP
Mass	128.5	33.5	35.3	144.4	55.2	48.4	116.1	32.2	28.4	149.1	36.5	55.8	86.7	19.3	45.8
Al	-	.38	1.61	-	1.39	2.44	-	.47	1.53	-	1.48	2.83	-	1.18	2.01
Si	-	.64	2.85	-	1.54	6.22	-	.67	3.22	-	2.51	6.96	-	1.01	4.93
S	-	3.29	1.05	-	3.32	.53	-	2.75	.35	-	2.47	.65	-	2.15	.49
Cl	-	.28	1.02	-	1.59	1.61	-	.15	.12	-	.74	1.77	-	.14	.70
K	-	.40	.22	-	.81	.50	-	.17	.21	-	.42	.95	-	.18	.53
Ca	-	1.08	2.72	-	1.11	6.05	-	.68	3.39	-	1.25	6.43	-	.69	2.86
Ti	-	.03	.05	-	.05	.12	-	.02	.05	-	.05	.15	-	.03	.05
V	.04	-	-	.06	-	-	[a]	-	-	.03	-	-	[a]	-	-
Cr	.01	-	-	.03	-	-	.01	-	-	.02	-	-	.01	-	-
Mn	.37	.04	.06	.28	.05	.11	.10	.03	.02	.10	.03	.04	[a]	.01	.02
Fe	7.10	.87	1.68	5.07	.69	2.79	2.11	.34	.72	2.73	.29	1.83	1.67	.26	.67
Ni	.03	.01	[a]	.02	.02	.01	[a]	[a]	[a]	.02	.01	[a]	.01	.01	[a]
Cu	.35	.03	.03	.81	.05	.07	.54	.05	.09	.75	.07	.06	.54	.03	.10
Zn	-	.11	.06	-	.36	.29	-	.22	.09	-	.17	.06	-	.04	.02
Br	-	.09	.02	-	.17	.04	-	.11	.03	-	.20	.06	-	.03	[a]
Sn	-	.05	.04	-	.05	.06	-	.05	.04	-	.05	.05	-	.05	.05
Pb	.91	.42	.12	1.16	.74	.21	.52	.49	.11	.89	.82	.24	.18	.15	.05
$SO_4^=$	20.8	9.6	1.9	20.7	10.4	7.0	11.2	8.2	.7	12.5	9.5	1.40	9.2	6.0	1.10
NO_3	6.11	1.79	1.23	5.29	1.70	1.37	1.90	.52	.68	17.62	6.89	3.35	3.56	3.95	1.33

[a]Not detectable.

With respect to the CP fraction, the geological chemical species dominate it at all site types in all cities. As would be expected, because of its larger particle size, the source contributions to chemical species in this size fraction should be more localized in nature, and consequently, more variable between sites.

Many other individual comparisons can be made, but a sufficient number have been made here to have addressed the source-oriented hypotheses advanced in Chapter 4. In nearly all cases, the average concentrations measured at the urban and background sampling sites support those hypotheses. At least some of the potential sources of FP and CP in the selected urban areas have been identified. It remains to quantify their contributions to ambient concentrations and to determine whether or not other sources must be sought to account for the mass concentrations measured at each site.

9.3 Urban-Scale Source Contributions

The chemical element balance receptor model was used to estimate the contributions of various sources in Buffalo, Houston, El Paso and Philadelphia to the FP and CP average mass concentrations presented in Tables 9.1.1 to 9.1.4. The model has been thoroughly explained elsewhere (Watson, 1979) and will not be elaborated on here.

The chemical element balance model, like any other model, is only a simplified representation of reality. The results it produces, therefore, must be considered in conjunction with its limitations. Its greatest limitation is the inadequacy of the input data on which it functions. These data include:

- The types of sources which could contribute to a receptor.
- The fractional chemical compositions of identified source types in the desired size fractions and valid estimates of their uncertainties. This fractional composition must be that which is perceived by the receptor, not necessarily that which is measured at the source.

- The chemical concentrations at the receptor in the desired size fractions and valid estimates of their uncertainties. These chemical species must be the same as those of the source emissions and the number of such species must exceed the number of source types.

The potential source types in each urban area were identified in Table 4.2.1. One difficulty which was noted in the discussion of this table was that many of these source types lack chemical species or other properties of their particulate matter emissions that allow them to be differentiated from each other. This effectively groups sources with similar compositions into the same source types. Some of the source types in Table 4.2.1 contain organic and elemental carbon as major constituents, and these species are not quantified on IP Network samples. Similarly, vanadium and chromium, which are species common to residual oil combustion and steel production, are not included in the IP Network data summaries. Sodium and ammonium are two other measurements which would aid in the attribution of receptor concentrations to marine or road salt and secondary aerosols, respectively; they are not routinely measured in the IP Network.

The source compositions of source types identified in Table 4.2.1 which were used to perform the chemical element balances are identified in Table 9.3.1. Most were taken from Watson (1979) because this is one of the few resources which reports most of the important chemical species in the FINE and COARSE size ranges with estimates of their uncertainties. Crustal shale, crustal limestone and steel industry compositions were taken from Dzubay (1980). Dzubay reports no uncertainties so arbitrary precisions of ±10% were assigned to each of his values. He does not segregate source compositions by particle size so the same values were used for chemical element balances on both the FINE and COARSE fractions. Because smelting was identified as a potential contributor in El Paso and Philadelphia, chemical analyses of copper smelting emissions from Zoller et al (1980) were adopted for the FP and CP fractions; the values used and the way they were calculated are included in Table 9.3.1. Unfortunately, no source compositions for lead smelting operations were available.

TABLE 9.3.1

SOURCE TYPES USED IN CHEMICAL ELEMENT BALANCES

Mnemonic	Source Type	Reference
CONTDUST	Continental Dust	Watson, 1979
DZCRUSTA	Crustal Material	Dzubay, 1980
DZLIMEST	Limestone	Dzubay, 1980
PAPHSOIL	Soil from Philadelphia	*
URBNDUST	Urban Dust	Watson, 1979
ALUMPROC	Aluminum Processing	Watson, 1979
DZSTEELI	Steel Industry	Dzubay, 1980
MARINE	Marine	Watson, 1979
PAPHMN	Mineral Industry	*
PBAUTOEX	Leaded Auto Exhaust	Watson, 1979
RESIDOIL	Residual Oil Combustion	Watson, 1979
FERROMAN	Ferromanganese	Watson, 1979
VEGBURN1	Vegetative Burn 1	Watson, 1979
VEGBURN2	Vegetative Burn 2	Watson, 1979
ZOLLERCU	Copper Smelting	Zoller et al, 1978*
ELEMENTC	Elemental Carbon from unidentified sources	Single Constituent Source
ORGANICC	Organic Carbon from unidentified sources	Single Constituent Source
NITRATE	Nitrate from unidentified sources	Single Constituent Source
SULFATE	Sulfate from unidentified sources	Single Constituent Source

*See next page.

TABLE 9.3.1 (Continued)

*SOURCE COMPOSITIONS UNIQUE TO THIS STUDY

PERCENT COMPOSITION

Chemical	FINE			COARSE		
Species	PAPHSOIL[b]	PAPHMN[c]	ZOLLERCU[d]	PAPHSOIL	PAPHMN	ZOLLERCU
Mass	100±10	100±10	100±10	100±10	100±10	100±10
OC	3.1±2.4	.61±6.4	a	1.4±.58	1.1±.26	a
EC	9.1±4.3	4.6±1.3	a	1.5±.69	2.4±.37	a
NO_3^-	.20±.15	.12±.17	a	.037±.015	.06±.021	a
$SO_4^=$	.53±1.3	.25±.35	60±6.0	.31±.19	.20±.082	60±6.0
Al	10±3.4	3.7±3.8	.86±.78	3.7±1.5	2.2±1.6	.86±.78
Si	22±8.5	5.2±2.1	a	12±4.5	3.8±1.0	a
S	.77±.053	5.2±.12	20±2.0	.25±.14	.40±.052	20±2.0
Cl	.32±.44	.32±.13	a	.027±.029	.20±.012	a
K	1.4±.71	.73±.081	a	.60±.20	.40±.087	a
Ca	3.0±3.2	.96±.021	a	2.2±1.3	.60±.068	a
Ti	.33±.19	.26±.071	a	.35±.10	.30±.0072	a
V	.014±.014	.14±.077	.0054±.0044	.0085±.01	.10±.017	.0054±.0044
Cr	.031±.033	.19±.026	a	.027±.038	.10±.001	a
Mn	.99±1.1	40±13	.0014±.0012	.38±.62	23±4.3	.0014±.0012
Fe	7.2±3.2	6.3±2.5	a	5.3±1.9	4.7±.002	a
Ni	.0082±.0054	.010±.0063	a	.0015±.0013	.01±.01	a
Cu	.040±.027	.030±.031	.61±5.0	.059±.084	.03±.014	6.1±5.0
Zn	.18±.19	.046±.042	6.6±9.5	.093±.094	.30±.006	6.6±9.5
Br	.0082±.0052	.0025±.0064	.0062±.0038	.0015±.0013	.0013±.006	.0062±.0038
Pb	.20±.13	.15±.029	.94±1.2	.044±.050	.10±.0064	.94±1.2

[a] Not detectable.

[b] Average of resuspended road dust samples taken from NW of NE transfer site, NW of NE waste site and SW of Allegheny Site.

[c] One soil sample taken around the manganese ore facility and 3 baghouse samples from the manganese ore facility in Philadelphia.

[d] Average of 5 samples from Zoller et al (1978) with sulfur concentrations arbitrarily set to 20% for each sample.

Source samples of a manganese ore handling operation and street dust were taken in Philadelphia as part of this study. These samples were dried, seived through a Tyler 400-mesh screen which eliminates particles with nominal diameters greater than 38 um, and resuspended for sampling with the SURE cyclone pre-separator, which was shown to yield a sample equivalent to the FP fraction, and an open-faced 47 mm filter. These samples were taken on Fluoropore Teflon filters for XRF and ion analyses and on quartz filters for carbon analysis. Four samples from the manganese ore facility and four soil samples were so analyzed and their fractional chemical compositions were calculated. The average and standard deviation of the four measurements for each chemical species were used for the source composition value and its uncertainty within each size fraction. Because the mass concentration of FINE particles was approximately one-tenth of that of the TOTAL particles in these samples, the TOTAL compositions were used for the COARSE compositions without correction for the FINE fraction. The resulting source compositions of PAPHMN and PAPHSOIL are presented in Table 9.3.1.

This selection of source compositions is admittedly inadequate for an application of the chemical element balance receptor model in four different cities. There is no reason to suppose that source compositions measured several years ago in Portland, Oregon, (Watson, 1979), soil compositions from a geochemistry handbook (cited by Dzubay, 1980), samples from five copper smelters in the southwestern United States (Zoller et al, 1978), a 1971 estimate of steel industry compositions (cited by Dzubay, 1980) and eight samples from two source types taken one year after the ambient sampling used in this study should closely approximate the source compositions perceived at the receptors in Buffalo, Houston, El Paso and Philadelphia between 1979 and 1980. The uncertainties associated with the source compositions specified in Table 9.3.1 are large, however, and it is hoped that they are sufficient to account for their lack of specificity. There may be significant discrepancies between the model results and the true source contributions.

Since the chemical element balance is based on a linear combination of source contributions it can be applied to average receptor concentrations to calculate average source contributions. The model equation is

$$C_{ik} = \sum_{i=1}^{p} a_{ij} S_{jk} \qquad 9\text{-}1$$

where the C_{ik} is the concentration of chemical species i in the kth receptor sample, S_{jk} is the contribution of the jth source to the kth receptor sample, and a_{ij} is the fractional quantity of species i in source j. Averaging over n samples yields

$$\overline{C}_i = \frac{1}{n} \sum_{k=1}^{n} C_{ik} = \frac{1}{n} \sum_{k=1}^{n} \sum_{j=1}^{p} a_{ij} S_{jk} = \sum_{j=1}^{p} a_{ij} \frac{1}{n} \sum_{k=1}^{n} S_{jk} = \sum_{j=1}^{p} a_{ij} \overline{S}_j \qquad 9\text{-}2$$

where $\overline{C}_i$ and $\overline{S}_j$ are the average concentrations and source contributions, respectively.

The precision of an average is equal to the standard deviation of the data set used to calculate it divided by the square root of the number of samples in it. The average concentrations presented in Tables 9.1.1 to 9.1.4 with their associated precisions were used as input to the effective variance least squares fit of source contributions to the chemical element balance equations. This fitting method propagates the uncertainties of the source compositions and the receptor concentrations through the solution process to provide estimates of the uncertainties of the source contributions. Because of the small number of values in some of the average concentrations and because of extreme values for some of the measurements used to obtain them, the width of the precision intervals associated with them might be underestimated. Thus, due to recognized limitations associated with the source and chemical composition data available to the chemical element balance receptor model, the source contributions calculated here are meant to be illustrative rather than conclusive.

Each chemical element balance was performed using the interactive, iterative process described by Watson (1979) using his criteria for the best least squares fit of source contributions to the chemical element balance equations. The combination of sources finally selected after various trials was that for which:

- The ratios of chemical concentrations calculated from Equation 9-1 to the measured concentrations most closely approached unity.
- The sum of the source contributions most closely approached the measured mass concentration.

Source types in a particular fit were selected from the set in Table 9.3.1 regardless of whether or not such a source type was listed in Table 4.2.1 as existing in the urban area under study. This was done for two reasons:

- Source types similar in composition to those included in the fit but not included in Table 4.2.1 may exist. Such sources should be sought, their true composition should be determined, Table 4.2.1 should be corrected and the balances should be re-run with the new source composition.
- If such source types do not exist in the area under study, the fact that they appear to be contributors raises legitimate doubts regarding the validity of the receptor model input data.

Any source contributions which were less than their associated uncertainties were removed from the fit. Normally all chemical concentrations were included in the fit except sulfur, because it duplicated the role of sulfate, and those below detection limits as indicated in Tables 9.1.1 to 9.1.4. The single constituent source types (Watson, 1979) in Table 9.3.1 are meant to show that portion of the chemical species they represent which is not accounted for by other source types. In the case of sulfate and nitrate this is an upper limit on the aerosol which forms in the atmosphere from emissions of sulfur and nitrogen-containing gases. For organic and elemental carbon this represents the upper limit of contributions from many sources, such as biological material and natural gas combustion, for which carbon is the major, and sometimes the only, constituent. Between five and ten iterations of different source type and chemical concentration combinations were required before the best fit was achieved. These iterations were performed by a technically qualified person whose only training in receptor models was that received at one of EPA's receptor model workshops; the purpose was to simulate the type of application which would normally take place for compliance modeling purposes. The specific details of all chemical element balances presented here can be obtained from the authors on request.

The results of the chemical element balances applied to the average chemical concentrations at sites in each of the four cities appear in Tables 9.3.2 to 9.3.5. The sum of all the average source contributions and the fraction of the measured mass that they account for are included in the final rows of the tables. For site types with a full complement of IP Network chemical concentrations, 60 to 70% of the average FP mass and 80 to 130% of the CP mass is accounted for. The exception for the FP mass occurs at NE Airport in Philadelphia and for the CP at Clint near El Paso.

The source contributions in these tables need to be examined for their consistency with the known source types in each urban area recorded in Table 4.2.1 and with the observations of Section 9.2.

The geological source types are most dominant in the CP fraction at all sites in all areas. In general, between 50 and 95% of the sum of the source contributions can be attributed to geological material. None of the four geological source compositions seems to be preferred by the fitting procedure at any particular site. Philadelphia's soil composition fits the COARSE chemical concentrations in Buffalo and El Paso better than it does those in Philadelphia.

Geological CP fraction source contributions at the urban sites are invariably elevated over similar contributions at corresponding urban-scale background sites, showing that some portion of the difference must be coming from local sources. It appears that even though size-classified sampling may eliminate some of the fugitive dust contributions which have so often lead to violations of standards with HIVOL samplers, geological material from a myriad of sources will still be a major contributor to inhalable particulate matter concentrations.

Unaccounted for sulfate is by far the largest contributor to the FP fraction though its presence in the CP fraction is small in all

TABLE 9.3.2

AVERAGE SOURCE CONTRIBUTIONS TO FINE AND COARSE PARTICULATE MATTER IN BUFFALO, NY

AVERAGE FINE SOURCE CONTRIBUTIONS (ug/m^3)

	Sampling Site			
Source Type	(1) P.S. No. 26 NYBUA	(2) Big Sister (NYBUB)	(3) P.S. No. 28 (NYBUC)	(4) Wilmuth Pump (NYBUD)[a]
Geological				
DZLIMEST	.83±.36	b	1.5±.5	
DZCRUSTA	b	b	b	
PAPHSOIL	b	2.3±.48	2.3±.6	
Secondary				
SULFATE	9.0±1.8	5.8±1.2	6.4±1.7	
NITRATE	1.7±.5	.51±.26	1.3±.5	
Other				
PBAUTOEX	2.0±.3	b	1.6±.4	
RESIDOIL	.18±.06	b	b	
VEGBURN2	2.9±1.4	.63±.29	3.7±1.8	
DZSTEELI	.64±.28	b	.95±.51	
ZOLLERCU	.50±.40	b	b	
PAPHMN	b	b	.46±.35	
Total:	20.3±2.5	10.3±1.3	18.1±2.7	
Percent of Measured Mass:	61±8%	61±9%	67±11%	

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[a] Insufficient data.
[b] Not needed in the fit.

TABLE 9.3.2 BUFFALO, NY (Continued)

AVERAGE COARSE SOURCE CONTRIBUTIONS (ug/m^3)

Source Type	Sampling Site (1) P.S. No. 26 (NYBUA)	(2) Big Sister (NYBUB)	(3) P.S. No. 28 (NYBUC)	(4) Wilmuth Pump (NYBUD)[a]
Geological				
DZLIMEST	7.2±.2.0	1.3±.3	7.3±1.9	
CONTDUST	b	2.2±.3	b	
PAPHSOIL	23.0±4.3	b	b	
URBNDUST	b	b	4.6±1.0	
Secondary				
SULFATE	1.4±.6	.54±.07	.59±.19	
NITRATE	.92±.15	.33±.07	b	
Other				
PBAUTOEX	.46±.11	.10±.02	.21±.07	
RESIDOIL	b	b	.15±.07	
MARINE	2.4±1.0	b	b	
DZSTEELI	b	.20±.03	1.5±.5	
VEGBURN1	b	b	12.1±3.2	
VEGBURN2	b	.44±.21	b	
ZOLLERCU	b	b	b	
ALUMPROC	b	2.0±.5	.85±.62	
Total:	36.0±5.0	7.1±.7	27.3±4.0	
Percent of Measured Mass:	122±19%	128±14%	108±18%	

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[a] Insufficient data.

[b] Not needed in the fit.

TABLE 9.3.3

AVERAGE SOURCE CONTRIBUTIONS TO FINE AND COARSE PARTICUALTE MATTER IN HOUSTON, TX

AVERAGE FINE SOURCE CONTRIBUTIONS (ug/m^3)

Source Type	Sampling Site (1) CAMS 8 (TXHOA)	(2) CAMS 1 (TXHOB)[a]	(3) Seabrook (B) (TXHOC)
Geological			
DZLIMEST	.75±.29		.91±.33
PAPHSOIL	2.0±.6		1.5±.4
Secondary			
SULFATE	8.7±1.5		5.8±1.8
NITRATE	.37±.08		.64±.2
Other			
PBAUTOEX	1.3±.4		b
RESIDOIL	.18±.10		b
VEGBURN2	1.2±.7		1.5±.8
ZOLLERCU	.60±.45		.18±.14
Total:	15.1±2.7		10.8±2.1
Percent of Measured Mass:	87±26%		76±24%

AVERAGE COARSE SOURCE CONTRIBUTIONS (ug/m^3)

Source Type	Sampling Site (1) CAMS 8 (TXHOA)	(2) CAMS 1 (TXHOB)[a]	(3) Seabrook (B) (TXHOC)
Geological			
DZLIMEST	4.8±1.7		6.1±1.6
CONTDUST	b		6.0±.9
PAPHSOIL	8.2±2.2		b
Secondary			
SULFATE	1.6±.10		.88±.36
NITRATE	1.1±.4		1.3±.3
Other			
PBAUTOEX	.34±.10		.14±.03
RESIDOIL	.18±.10		b
MARINE	3.3±1.6		2.0±.9
Total:	19.7±3.4		16.5±2.0
Percent of Measured Mass:	116±32%		90±19%

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[a] Insufficient data.

[b] Not needed in fit.

TABLE 9.3.4

AVERAGE SOURCE CONTRIBUTIONS TO FINE AND COARSE PARTICULATE MATTER IN EL PASO, TX

AVERAGE FINE SOURCE CONTRIBUTIONS (ug/m^3)

Source Type	Sampling Site	
	(1) El Paso (TXELA)	(2) Clint (B) (TXELB)
Geological		
DZLIMEST	2.2±.6	1.3±.2
PAPHSOIL	2.5±.6	b
URBNDUST	b	2.6±.3
Secondary		
SULFATE	1.4±.17	2.3±.6
NITRATE	.36±.32	.51±.13
Other		
PBAUTOEX	3.3±.9	.65±.15
VEGBURN2	3.7±2.0	1.0±.5
ZOLLERCU	1.0±.6	.33±.24
PAPHMN	b	.012±.004
Total:	14.6±2.6	8.7±.9
Percent of Measured Mass:	63±18%	71±9%

AVERAGE COARSE SOURCE CONTRIBUTIONS (ug/m^3)

Source Type	Sampling Site	
	(1) El Paso (TXELA)	(2) Clint (B) (TXELB)
Geological		
DZLIMEST	21.8±5.7	8.8±1.4
CONTDUST	13.7±2.4	b
Secondary		
SULFATE	b	.41±.21
NITRATE	.46±.16	.42±.12
Other		
PBAUTOEX	.89±.30	.21±.07
VEGBURN2	b	2.1±1.0
ZOLLERCU	.94±.21	.31±.25
ALUMPROC	b	3.5±1.2
MARINE	.53±.22	b
Total:	38.3±6.1	27.0±2.5
Percent of Measured Mass:	82±17%	59±8%

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[a] Insufficient data.

[b] Not needed in fit.

TABLE 9.3.5

AVERAGE SOURCE CONTRIBUTIONS TO FINE AND CORASE PARTICULATE MATTER IN PHILADELPHIA, PA

AVERAGE FINE SOURCE CONTRIBUTIONS (ug/m^3)

	Sampling Site				
Source Type	(14) 500 S. Broad (PAPHA)	(1) Allegheny (PAPHB)[a]	(2) St. John's (PAPHI)[a]	(1) Pres. Home (PAPHG)	(10) NE Airport (B) (PAPHE)
Geological					
DZLIMEST	b			.48±.24	.39±.24
DZCRUSTA	4.8±.8			b	b
PAPHSOIL	b			1.9±.5	2.1±.4
Secondary					
SULFATE	c			10.0±2.3	6.1±.9
NITRATE	c			.57±.17	.46±.15
Other					
PBAUTOEX	3.0±.76			3.1±.7	1.8±.4
RESIDOIL	.53±.20			b	.18±.06
DZSTEELI	b			b	b
ZOLLERCU	.99±.83			.27±.23	.47±.34
VEGBURN2	b			1.2±.6	.78±.39
PAPHMN	b			b	b
Total:	9.4±1.4			17.9±2.6	12.2±1.2
Percent of Measured Mass:	40±7%			58±10%	53±6%

[a] Insufficient data.
[b] Not needed in fit.
[c] Not included due to lack of data.

TABLE 9.3.5 PHILADELPHIA, PA (Continued)

AVERAGE COARSE SOURCE CONTRIBUTIONS (ug/m^3)

Source Type	Sampling Site (14) 500 S. Broad (PAPHA)	(1) Allegheny (PAPHB)[a]	(2) St. John's (PAPHI)[a]	(1) Pres. Home (PAPHG)	(10) NE Airport (B) (PAPHE)
Geological					
DZLIMEST	4.0±1.6			2.4±.5	1.4±.3
CONTDUST	18.0±2.4			7.1±.8	5.3±.5
Secondary					
SULFATE	c			.96±.21	.57±.16
NITRATE	c			.74±.17	.67±.12
Other					
PBAUTOEX	.95±.23			.78±.16	.45±.09
RESIDOIL	.15±.10			.12±.06	b
ZOLLERCU	.59±.48			b	.21±.16
MARINE	.95±.47			.43±.19	.74±.35
PAPHMN	.044±.040			.049±.017	.017±.008
ALUMPROC	b			1.31±.68	1.3±.45
Total:	24.7±3.0			14.0±1.2	10.7±.9
Percent of Measured Mass:	131±19%			83±9%	79±8%

[a] Insufficient data.
[b] Not needed in fit.
[c] Not included due to lack of data.

urban areas except El Paso. This is consistent with other observations in the eastern United States (Mueller and Hidy et al, 1981; Dzubay, 1980). The FP sulfate is usually considered to be regional in nature, though the contributions at urban sites in Buffalo, Houston and Philadelphia are significantly higher than those at the corresponding background sites, usually by a factor of 1.5 to 2. This could be due to chemical concentration averages calculated from non-simultaneous samples at the different sites, some of which might include more sulfate-rich days than others; it could also be due to other sources of sulfate within the urban area which need to be identified. El Paso experiences low unaccounted for sulfate contributions even though the smelter is a major source of SO_2. No regional-scale pollution episodes are known to affect El Paso as have been documented for Buffalo and Philadelphia (Mueller and Hidy et al, 1981).

Unaccounted for nitrate is generally evenly distributed between FP and CP fractions and is not substantially elevated over background levels except at P.S. 26 in Buffalo where the FP nitrate is nearly twice the CP nitrate and three times the background value. The nitrate source contribution appears to be of a regional scale and of a small (less than 1 ug/m^3) magnitude.

The other source types appear to follow the expectations of Table 4.2.1 with respect to dominant particle size and play subordinate roles to geological material in the CP fraction and, with the exception of El Paso, to unaccounted for sulfate in the FP fraction.

Leaded auto exhaust is a familiar contributor at most urban sites with contributions on the order of 2 to 3 ug/m^3. The PBAUTOEX contribution in El Paso may be elevated over its true value by accounting for some of the lead from the lead smelter; it will be recalled that no source composition for lead smelters was used in the chemical element balances.

The residual oil combustion contributions are generally very small (less than .2 ug/m^3) if present at all, but without a vanadium concentration this source type is most sensitive to nickel concentrations, and these are often at or below detection limits.

The MARINE contributions in Buffalo, Houston and Philadelphia are in the CP fraction, are elevated with respect to background sites and are 1 to 3 ug/m^3 of the COARSE mass. Because they are so much higher at inland sites, the source is probably not so much marine as it is some sort of salting activities. A source composition for this source type should be obtained. There may be other urban sources of chlorine in these cities which could also be contributors; it is improbable that much road salt would be applied in Houston. Chemical element balances for summer and winter averages might help to resolve the issue. The small CP MARINE contribution in El Paso might be mistaken for vegetative burning which is also sensitive to chloride concentrations.

The VEGBURN1 and VEGBURN2 contributions are among the most tenuous of all the sources. Watson (1979) expressed grave doubts about the representativeness of the measurements made to obtain his source compositions, and the only reason he included them in chemical element balances was because they accounted for much of the organic carbon measured on Portland's aerosol samples. The vegetative burning source contributions are sensitive to chlorine and potassium concentrations. At P.S. 28 in Buffalo, for example, a CP MARINE contribution would probably be more consistent with other sites, and reality, than the 12 ug/m^3 vegetative burning contribution without significantly deteriorating the quality of the fit. In general, however, the vegetative burning contributions are concentrated in the FP fraction, where they belong, are of a reasonable magnitude, 1 to 4 ug/m^3, and are highest in Buffalo and El Paso, where heating by wood burning is a likely possibility. The contributions from this source type must be considered as speculative.

The industrial process contributions must also be considered to be speculative. For the most part the steel, copper smelter, aluminum processing and manganese ore handling source types are small contributors (less than .5 ug/m^3 apiece to either size fraction) and, because their source compositions are usually dominated by one chemical species, they are probably just filling in small differences between measured and calculated concentrations for those species, similar to the role played by the single constituent source types.

The exceptions are in Buffalo, where steel industry contributions approach 1 ug/m^3 in the FP fraction and where this industry is expected to affect the urban sampling sites. Even if this contribution is real, however, it is not a major contributor to either size fraction and, consequently, to average IP concentrations.

Several individual samples from Philadelphia were chosen from the IP Network archives for non-routine analyses. The purpose of these analyses were twofold. They were intended to see whether or not any advantage could be gained from analytical methods not part of the IP Network analyses, in this case carbon and optical microscopic analyses, and to further test the validity of the chemical element balance receptor model by applying it to individual samples taken simultaneously at different sites. In order to perform carbon analysis on HIVOL and SSI filters it was necessary to choose samples from 1979, prior to the use of the S&S filter described in Chapter 3. Unfortunately, sampling problems severly limited the number of simultaneous samples available so that, out of the ten sampling sites operating in Philadelphia during the latter part of 1979, only two at a time yielded simultaneous dichotomous samples. Up to five sites at a time yielded SSI samples. Sulfate, nitrate and carbon measurements were made on HIVOL or SSI quartz fiber filters while elements were measured on the FINE and COARSE Teflon filters. The sulfate, nitrate and carbon concentrations were placed in the FINE size category because their concentrations are usually highest in that fraction; in reality these measurements are a combination of concentrations in both the FP and CP fractions.

October 18, 1979 and November 20, 1979 were days with very high IP concentrations in Philadelphia. The measured mass for each sample in the final row of Table 9.3.6 shows that most of the IP mass was in the FP fraction on these days. November 17, 1979 showed IP concentrations which were within the typical urban ranges observed in Chapter 5.

On October 18, 1979, the major contributors to the FINE fraction were auto exhaust and unaccounted for sulfate. The auto exhaust contribution was several times larger than that found for the average source contributions in Table 9.3.5. The FINE geological, unaccounted

TABLE 9.3.6

SOURCE CONTRIBUTIONS (ug/m^3) ON INDIVIDUAL SAMPLING DAYS IN PHILADELPHIA, PA

Source Type:	Oct. 18, 1979				Nov. 17, 1979				Nov. 20, 1979			
	FINE		COARSE		FINE		COARSE		FINE		COARSE	
	(11)Pres. Home PAPHG	(6)NE Transfer PAPHM	(11)Pres. Home PAPHG	(6)NE Transfer PAPHM	(1)500 S. Broad PAPHA	(10)NE Airport PAPHE	(1)500 S. Broad PAPHA	(10)NE Airport PAPHE	(11)Pres. Home PAPHG	(10)NE Airport PAPHE	(11)Pres. Home PAPHG	(10)NE Airport PAPHE
Geological												
DZLIMEST	b	1.3±.3	4.9±.8	b	b	b	5.6±.7	2.0±.3	.52±.23	b	4.0±.8	1.0±.3
CONTDUST	b	4.1±.6	16.5±1.2	48.7±3.2	b	b	11.1±.6	5.8±.4	2.1±.3	b	20.2±1.5	b
URBNDUST	b	b	b	b	2.9±.2	1.1±.1	b	b	b	6.1±.4	b	29.2±1.2
PAPHSOIL	3.8±1.0	b	b	b	b	b	b	b	b	b	b	b
MARINE	b	b	b	b	b	b	.2±.07	.2±.07	b	b	b	b
Secondary												
SULFATE	16.6±1.8	10.8±1.3	c	7.4±1.4	12.0±1.2	1.2±.5	4.1±.5	c	40.8±4.2	25.4±2.7	c	6.3±1.1
NITRATE	.08±.2	9.0±.9	c	c	.4±.05	.1±.05	c	c	.36±.05	.19±.04	c	c
ORGANICC	5.3±2.4	4.1±1.4	c	c	5.9±.8	c	c	c	8.1±1.5	3.5±1.1	c	c
ELEMENTC	5.8±1.0	3.3±.7	c	c	3.1±.7	c	c	c	14.2±1.5	9.3±1.1	c	c
Other												
RESIDOIL	.7±.2	.5±.10	.2±.04	.3±.08	.9±.1	.4±.09	.4±.08	.3±.09	2.0±.5	4.0±.6	.90±.22	1.6±.3
PBAUTOEX	11.2±1.8	10.5±1.5	2.4±.4	2.1±.4	3.4±.5	4.2±.6	1.3±.2	.9±.2	10.3±1.4	7.5±1.1	2.0±.3	2.4±.4
ZOLLERCU	1.0±.7	1.8±1.3	.7±.5	1.9±1.4	.5±.3	1.1±.8	.3±.2	.7±.1	2.6±1.9	1.5±1.1	.87±.60	1.8±1.3
PAPHMN	.001±.1	.1±.04	b	b	.03±.01	.04±.02	.03±.02	.01±.009	.11±.04	.14±.04	b	b
VEGBURN2	5.3±3.7	b	b	b	b	1.4±.7	b	b	b	b	b	b
ALUMPROC	b	b	b	b	b	b	b	1.1±.5	b	b	b	b
Total:	49.8±5.3	45.4±3.1	24.8±1.6	60.5±3.8	29.1±1.7	9.6±1.3	23.1±1.1	11.1±.8	81.0±5.3	57.7±3.6	27.9±1.9	42.2±2.1
Percent of Measured Mass:	79±11%	62±8%	73±9%	234±28%	107±12%	44±8%	78±9%	96±12%	72±8%	64±7%	82±9%	96±10%
Measured Mass:	63.2	73.0	34.0	25.8	28.3	21.7	29.5	11.6	112.2	90.3	34.1	43.7

[a] Insufficient data.

[b] Not needed in fit.

[c] Not included due to lack of data.

for organic carbon, unaccounted for elemental carbon, residual oil combustion, auto exhaust and copper source contributions were uniformly distributed (i.e. the uncertainty intervals of each contribution overlap) among the two sites. The manganese ore handling contribution at NE Transfer was consistent with its location relative to both sites in Figure 4.2.7. The FINE unaccounted for sulfate contribution near Presbyterian Home was significantly greater than that at NE Transfer on October 18, 1979; this source contributed more to the FINE mass concentrations at Presbyterian Home than at NE Airport on the other days examined and on the average, as shown in Table 9.3.5. It is not obvious where this additional sulfate came from. Since sulfate was measured on glass fiber filter media for the individual days an artifact problem is possible, though samples taken in 1979 should not be susceptible to this.

The large differences between unaccounted for nitrate and vegetative burning contributions to the two sites is not consistent with the area-wide emissions nature of these sources.

In the COARSE sample, contributons of geological material dominated at both sites, though the contribution at NE Transfer was much higher than the CP mass measurement there; since all chemical species in the chemical element balance fit for this sample showed relative concentrations which were consistent with each other, it is suspected that the filter which was analyzed and its mass concentration do not correspond to each other.

On November 17, 1979, the FINE sample at 500 S. Broad showed higher contributions from geological material similar to that found in Table 9.3.5. The unaccounted for carbon contributions were also much higher. Residual oil combustion, copper smelting and manganese ore handling contributions were low and did not differ significantly between sites, which is consistent with previous observations that they are part of the noise in the measurements. The auto exhaust contribution at 500 S. Broad should have been greater than that at NE Airport but the FINE chemical element balances did not show this. Once again, geological material dominated the COARSE fraction.

On November 20, 1979, auto exhaust and unaccounted for sulfate were major contributors to the FINE mass. The residual oil combustion contributions were higher than any others observed at both sites; if November 20 were a very cold day, this would make sense because of the proximity of residual oil burning sources to these sites shown in Figure 4.2.7. The COARSE fraction, once again, was dominated by geological material.

The comparison of source contributions to simultaneous samples at different sampling sites coupled with a knowledge of the geographical relationships between source and receptor locations aids the acceptance or rejection judgement to be made for each chemical element balance. The examples in Table 9.3.6, limited though they are, show that conclusions about measurement validity, unidentified sources, and the real (as opposed to the estimated) lower quantifiable limits for source contributions can be drawn from these comparisons.

The carbon measurements did not add much value to the balances; the fractions of the FINE mass concentrations accounted for did not increase significantly over those which were found without carbon measurements. The use of carbon concentrations in this application is crude, however, due to the lack of a filter medium for FINE and COARSE samples which is amenable to carbon analysis.

The source contributions to the COARSE fractions of IP have not exhibited great variety; geological material has been the major contributor. A more detailed examination of contributions to this fraction in Philadelphia using optical microscopy is presented in Table 9.3.7. Unfortunately, in only one case, 500 S. Broad on November 17, 1979, were SSI, FINE and COARSE samples available simultaneously.

Comparing the COARSE source contributions to these samples from Tables 9.3.6 and 9.3.7 shows that while the chemical element balances calculate a 57% contribution from geological sources, the microscopic analysis shows only 22.5% due to minerals. The chemical element balance biological and combustion sources are negligible whereas these sources constitute 50% and 26%, respectively, of the CP fraction according to microscopic analysis results. The more specific groupings of the microscopic analysis (Crutcher and Nishimura, 1981)

TABLE 9.3.7

RESULTS OF MICROSCOPIC ANALYSIS OF CP ON SELECTED SSI SAMPLES IN PHILADELPHIA, PA

Location	Sampling Date	Composition, Percent of COARSE					SSI ug/m^3
		Minerals	Biologicals	Industrial & Transportation	Combination	Other	
500 S. Broad	Oct. 18, 1979	20.2	41.7	5.6	32.5	0	119
Allegheny		29.5	27.1	12.6	30.7	.1	95
St. John's		43.8	15.0	16.6	24.6	0	90
Pilot Freight		26.7	30.5	10.3	32.5	0	137
NE Waste		33.9	41.0	12.1	12.9	0	-
500 S. Broad	Nov. 8, 1979	20.0	38.2	5.6	36.2	0	44
Allegheny		13.5	56.0	5.5	25.0	0	83
St. John's		26.1	21.5	14.6	37.8	0	76
Pilot Freight		53.1	11.9	9.2	25.8	0	102
NE Waste		24.6	37.1	5.2	33.1	0	62
500 S. Broad	Nov. 17, 1979	22.5	49.6	1.0	26.1	.8	62
500 S. Broad[a]		19.3	36.5	9.5	34.7	0	62
Allegheny		26.9	36.9	28.0	18.1	.1	102
St. John's		18.6	27.7	14.1	37.6	2.0	54
Pilot Freight		28.7	22.5	15.4	26.1	7.3	69
Pilot Freight[a]		29.7	30.3	12.8	27.1	.1	69
NE Waste		15.3	51.5	5.8	27.4	0	50
NE Waste[a]		22.0	41.0	15.3	20.4	1.3	50
500 S. Broad	Nov. 20, 1979	20.6	20.2	23.4	35.8	0	160
Allegheny		39.2	8.9	30.5	21.4	0	167
St. John's		50.4	6.7	15.1	27.8	0	175
Northeast Waste		19.3	29.1	16.6	26.2	8.8	161

[a] Replicate analysis of the same slide by a different microscopist

showed most of the biological material was present as plant parts (17% of total mass) and other biologicals (20%) and most of the combustion products as charred wood (19%).

These major differences in source contributions to the same sampling site at the same time cast doubt not only on the source contribution estimates but on the methods of achieving them.

One source of this difference may rest with the limitations of these methods. The limitations of the input data to the chemical element balance were discussed in this section and those of the optical microscopic analysis were presented in Section 3.3. The replicate microscopic analyses of samples offers an estimate of the uncertainty associated with each of these measurements. These replicate analyses were performed by different microscopists on the same slides prepared from SSI filters taken at 500 S. Broad, Pilot Freight and NE Waste on November 17, 1979. The results of the contributions to the five general categories are included in Table 9.3.7. The most notable feature of these replicates is that when the contribution of one category drops below 15 to 20%, the replicates exhibit extreme differences; industrial and transportation at 500 S. Broad and NE Waste, and the "other" category at Pilot Freight are the most striking examples. Significant deviations at higher contribution levels are also present, notably in the biological and combustion contributions to NE Waste.

These differences become larger when the specific categories of Crutcher and Nishimura (1981) are compared. At 500 S. Broad, Nishimura found 27% of the CP fraction composed of plant parts and 20% other biologicals while Crutcher, examining the same sample, found 23% due to plant parts and only 3% contributed by other biologicals. In combustion products, Nishimura estimated that 19% of the CP mass was due to charred wood with only 3% from fused flyash while Crutcher found that 18% was contributed by fused flyash with only 2% coming from charred wood. Similar differences showed themselves at NE Waste and Pilot Freight. These detailed summaries are available upon request to the authors of this report.

Replicate analyses of chemical compositions of selected samples always showed agreement within ±10% for concentrations greater than ten times the lower quantifiable limit. To estimate the true uncertainty associated with chemical element balance source contributions, however, the entire modeling process should be duplicated by different researchers. Each should choose the source types and their compositons independently of the other and each should perform the chemical element balance fitting procedures using his choice of chemical species and sources. Only after this procedure is followed and the source contributions calculated from the same chemical measurements compared will the process be similar to that performed by two separate microscopists looking at the same sample.

Major differences between the two methods will probably persist, however, for the CP fraction simply because the geological source compositions do not vary by great amounts; it is likely that greater than 50% of the CP fracton will be attributed to geological material whereas the results in Table 9.3.7 show most of this material contributing in the 20 to 30% range. The biological, industrial, transportation and combustion source types appear to be major contributors by microscopic analysis, but their contributions via chemical element balances are much smaller.

Certainly more work needs to be done to perfect both methods and to evaluate their applicability to estimating source contributions from IP Network samples.

The treatment here, which is a small part of a moderate-sized study, cannot be expected to resolve all of the problems and inconsistencies which have been noted; however, these efforts do suggest an iterative scenario which could be followed to provide a cost-effective yet defensible estimate of source contributions. The steps would include:

1. Identify and locate likely source types contributing to an area's air using existing emissions inventories.
2. Use whatever source compositions are available, even if their source types do not exist in the area under study, to perform chemical element balances on average and selected individual chemical concentrations.

3. Compare simultaneous source contributions from different sites with each other and with the proximity of sources to receptors documented in Step 1. Eliminate those localized source types which make small but uniform contributions over a large area.

4. Obtain source samples from source types in the area under study which have been identified as possible contributors. Submit these to chemical and microscopic analysis.

5. Reanalyze those receptor and source samples for which chemical compositions seem inconsistent.

6. Run chemical element balances with new sources. Perform microscopic analyses of selected samples using a standardized methodology and use chemical element balance fitting procedures with microscopic concentrations and source compositions to determine source contributions.

Though this procedure should help to refine the source contribution estimates, the analysis in this section strongly suggests three things:

- The greatest contributors to average and high FP mass concentrations in the eastern United States are unaccounted for sulfate (possibly due to the conversion of SO_2) and, secondarily, automobile exhaust.
- The greatest contributions to CP concentrations are from geological material.
- Industrial point sources generally make small contributions to average and elevated IP mass concentrations.

These observations are based on the very tenuous assumptions already stated about the receptor models used and need to be verified using the steps which have been proposed in this section.

These observations apply to urban-scale measurements, but in many cases source emissions may be clustered in such close proximity to each other that the source contributions estimated at one site may not be completely representative of the neighborhood under study. A neighborhood-scale sampling network is necessary to ascertain the variability across an industrial neighborhood.

9.4 Neighborhood-Scale Source Contributions

In an urban-scale compliance monitoring program, one sampling site is used to represent an entire neighborhood. Though the TSP, IP and FP concentrations measured at this station may be representative of the area as a whole, the source contributions to the concentrations measured at that station may not be the same as the source contributions to an equal mass concentration measured at another station in the neighborhood.

To study this issue, the samples collected in the Bridesburg industrial neighborhood of Philadelphia, depicted in Figure 4.2.8 are used. Each of the seven Bridesburg sampling sites was intended to take 24-hr samples every third day. Due to technical difficulties, this intended sampling program was not completely carried out. Unfortunately, sites having SSI measurements had incomplete dichotomous measurements and sites with a whole set of dichotomous measurements lacked complete SSI data. Only three Bridesburg sites, T&A Pet Shop (5), NE Transfer (6) and Bridesburg Recreation Center (7) yielded enough dichotomous samples for x-ray fluorescence analysis. These three sites are on the perimeter rather than in the core of the Bridesburg neighborhood. NE Airport (10), the urban-scale background site, also provided a number of dichotomous samples on which measurements could be made. These samples were taken between 10/3/79 and 2/15/80. The same type of analysis applied to urban-scale chemical concentrations in the first three sections of this chapter can be applied to the neighborhood-scale concentrations in Bridesburg.

Table 9.4.1 presents the average and maximum mass and elemental concentrations of FP and CP measured at the three sampling sites. There are no significant differences among these sites in the FP averages for mass, Al, Si, S, K, Ca, Ti, Ni, Br, and Pb. Similarly, in the CP averages, the concentrations of mass, S, Cl, K, Br and Pb are homogeneously distributed over the area encompassed by the Bridesburg perimeter samplers. Comparing these elements to those associated with the known sources in the Bridesburg area in Table 4.2.1 shows that the FP fraction might be equally affected by urban dust and motor vehicle exhaust at all sites. The CP fraction shows equal effects of motor vehicle exhaust at all sites.

TABLE 9.4.1

AVERAGE AND MAXIMUM CHEMICAL CONCENTRATIONS IN THE BRIDESBURG INDUSTRIAL AREA OF PHILADELPHIA (10/79 - 2/80)

(Data from Chow et al, 1981)

FINE CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site							
Chemical Species	(5)T&A Pet (PAPHL) Avg	Max	(6)NE Transfer (PAPHM) Avg	Max	(7)BRC (PAPHN) Avg	Max	(10)NE Airport (B) (PAPHE) Avg	Max
Mass	29.70	(108.80)	32.50	(106.60)	29.10	(77.80)	21.00	(51.60)
Al	.36	(1.36)	.34	(.83)	.29	(.40)	.26	(.40)
Si	.35	(2.82)	.29	(.98)	.31	(1.19)	.30	(1.13)
S	2.65	(12.59)	2.70	(7.94)	2.58	(5.28)	2.52	(5.65)
Cl	.30	(1.50)	.67	(4.05)	.52	(3.24)	.12	(.50)
K	.20	(.62)	.18	(.36)	.18	(.39)	.13	(.23)
Ca	.30	(1.48)	.28	(.56)	.25	(.39)	.17	(.26)
Ti	.03	(.27)	.03	(.16)	.03	(.15)	.02	(.03)
Mn	.10	(.93)	.02	(.06)	.02	(.16)	.01	(.02)
Fe	.34	(2.48)	.25	(.78)	.20	(.47)	.14	(.26)
Ni	.02	(.11)	.02	(.09)	.02	(.04)	.01	(.03)
Cu	.02	(.10)	.14	(1.83)	.05	(.61)	.02	(.04)
Zn	.15	(.98)	.55	(7.17)	.19	(.93)	.09	(.25)
Br	.19	(.59)	.16	(.47)	.15	(.43)	.12	(.33)
Pb	.69	(1.82)	.66	(2.02)	.56	(1.81)	.53	(1.31)
$SO_4^=$		-		-		-		-
NO_3^-		-		-		-		-
No. of Observations:								
Mass		33		37		28		34
Elements		40		40		40		17
Ions		-		-		-		-

TABLE 9.4.1 BRIDESBURG, PA (Continued)

COARSE CHEMICAL CONCENTRATIONS (ug/m^3)

	Sampling Site							
	(5)T&A Pet (PAPHL)		(6)NE Transfer (PAPHM)		(7)BRC (PAPHN)		(10)NE Airport(B) (PAPHE)	
Chemical Species	Avg	Max	Avg	Max	Avg	Max	Avg	Max
Mass	20.80	(75.20)	23.00	(56.90)	21.50	(77.30)	10.06	(22.70)
Al	.95	(2.90)	1.55	(6.64)	1.10	(3.03)	.82	(1.33)
Si	1.89	(6.39)	2.79	(10.47)	2.10	(5.66)	1.46	(3.07)
S	.60	(7.01)	.56	(2.87)	.51	(2.16)	.31	(1.64)
Cl	.42	(2.86)	.40	(1.87)	.36	(1.98)	.27	(1.90)
K	.21	(.65)	.28	(1.09)	.21	(.58)	.15	(.28)
Ca	.88	(2.59)	1.30	(12.07)	.83	(2.14)	.55	(1.09)
Ti	.07	(.26)	.11	(.54)	.07	(.36)	.04	(.12)
Mn	.38	(6.85)	.05	(.32)	.03	(.12)	.02	(.04)
Fe	.96	(4.38)	1.17	(3.58)	.86	(2.16)	.56	(1.49)
Ni	[a]	(.05)	[a]	(.07)	[a]	(.02)	[a]	(.02)
Cu	.02	(.14)	.11	(1.17)	.03	(.18)	.01	(.03)
Zn	.12	(1.35)	.52	(6.99)	.14	(.79)	.05	(.15)
Br	.05	(.57)	.08	(.12)	.03	(.11)	.03	(.08)
Pb	.24	(2.03)	.20	(.84)	.15	(.36)	.13	(.28)
$SO_4^=$		-		-		-		-
NO_3^-		-		-		-		-
No. of Observations:								
Mass	33		37		28		34	
Elements	40		40		40		17	
Ions	-		-		-		-	

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[a] Not detectable.

The most striking information conveyed by Table 9.4.1 is in those average concentrations which show differences from site to site. FP Cu and Zn concentrations are 3 and 4 times higher at NE Transfer than they are at the other sites. This site is also the closest to the copper smelting (34) operations pictured in Figure 4.2.8. The highest Cu and Zn concentrations at this site are 6 and 8 times the average of the highest values at the other two sites. The second highest Cu and Zn concentrations at site 6 are 3 are 8 times the average of the highest values at sites 5 and 7 for FP. These few extremly high values shown in Table 9.4.1 at NE Transfer cause the average at that site to be higher than the averages at the other two sites. These highest values show that Cu and Zn concentrations are periodically higher at site 6 which is consistent with the concept of a point source which is sometimes upwind of a nearby receptor. Average FP Mn and Fe concentrations are 5 and 1.5 times higher, respectively, at site 5 than they are at the other two sites, and the highest values show that this is not a general phenomenon, but one that occurs on just a few days. Since Al and Si are not simultaneously elevated, it is unlikely that geological material is the contributor here. The close proximity of the manganese ore unloading facility (59) could explain this. The average FP Cl concentration at site 5 is only half as high as that at the other two sites; no single source of this element is identified by Table 4.2.1.

The lack of spatial homogeneity of several of the CP elemental concentrations is consistent with the contention that geological contributions vary from site to site. CP concentrations of Al, Si, Ca, Fe and Ti are approximately 1.5 times higher at site 6 than they are at the other two sites. This is consistent with the larger quantity of truck traffic at this site described in the site survey summary of Table 3.1.3. The elevated CP Cu and Zn levels at site 6 are consistent with the source/receptor relationship established for the corresponding FP concentrations. The high Mn concentration at site 5 is also consistent with that observed for the FP Mn. A corresponding elevation of the Fe concentration would be masked by the urban dust contributions.

It appears that local metallurgical sources and nearby resuspension of urban dust affect site 6 and that mineral handling affects site 5. It is interesting to note that the coke oven (40), with some of the highest emissions in the Philadelphia airshed according to the NEDS emissions inventory, does not show itself to be a contributor to sites 5 and 7 which are closest to it. A glance at Table 4.2.1 shows that carbon, which has not yet been measured, is the major chemical species to be expected from this source.

The average Bridesburg FP mass loading is 7.6 ug/m^3 higher than the urban-scale baseline FP mass. This difference accounts for 25% of the Bridesburg FP concentrations. Comparing elemental concentrations indicates local contributors to this increment. Most geologically related elemental concentrations (Al, Si, K, Ti) are not appreciably higher in Bridesburg than they are at NE Airport. Ca and Fe are slightly enriched (less than a factor of 2), but this is consistent with measurements of urban dust which show elements of concrete (Ca) and metal (Fe) abrasion (Hopke et al, 1980). Cu and Zn concentrations are higher at Bridesburg sites than at the urban-scale background site, supporting the contention that local sources are responsible. The doubling of Pb and Br concentrations from the urban-scale background to the industrial setting shows the importance of automobile exhaust as a local Bridesburg source of these elements. Sulfur (S), presumably in the form of sulfate, is homogenously distributed across the industrial and urban-scale background sites, confirming what is known of its regional nature. Though some of the Bridesburg Cl could be due to automobile exhaust, it is a factor of 4 or 5 times higher at two Bridesburg sites than it is in the urban-scale background average. There is an unidentified local source of this element in the area, possibly the salting of roads during the winter months of this sampling program.

For the CP, the average Bridesburg mass loading is 8.2 ug/m^3 higher than the average concentration; thus, local activities account for approximately 38% of the CP. The geologically related elements are the most highly enriched and urban dust is the most likely contributor to these increments. However, Table 4.2.1 shows a number of local emission sources in the CP mode which do not contain the elements for which measurements were made. Feed and grain handling, and coal and coke storage piles contain significant quantities of carbon in CP particles which may be part of the local contribution.

Automobile exhaust, urban dust, copper and possibly zinc operations appear to be among the local sources contributing to ambient concentrations, though there may be others whose chemical structure would show no affect on the chemical concentrations which have been measured to date.

Table 9.4.2 presents the chemical element balance source contributions calculated from the average concentrations in Table 9.4.1. These source contributions, for the most part, support the observations made from the chemical concentrations. FP source contributions in the Bridesburg area are fairly evenly distributed if one discounts the vegetative burning contributions which are probably due to the Cl concentrations; these might be better assigned to the marine aerosol, or more probably, road salt. The CP fraction shows higher geological contributions at NE Transfer, and a higher manganese ore handling influence at T&A Pet, both of which are consistent with the relative locations of sources and receptors.

The conclusions drawn from this neighborhood-scale study of the sources affecting FP and CP particulate matter concentrations in the Bridesburg industrial area are:

- Approximately 25% of the FP, 38% of the CP, and therefore, 30% of the IP average mass concentrations are contributed by local Bridesburg sources. This means that up to 70% of the average IP mass loadings are contributed by the urban-scale aerosol and are not subject to local control in Bridesburg.

- Both average FP and CP mass concentrations, and therefore IP concentrations, are homogeneously distributed over the three Bridesburg sampling sites.

- Average FP mass concentrations are almost equally affected by locally generated sources, though certain small mass contributors may have higher influence on certain chemical species.

- Average CP mass concentrations are uniformly distributed, but samplers in close proximity to local geological and ore handling sources show greater contributions from these source types.

TABLE 9.4.2

SOURCE CONTRIBUTIONS IN THE BRIDESBURG INDUSTRIAL AREA

AVERAGE FINE SOURCE CONTRIBUTIONS (ug/m^3)

Source Type	Sampling Site PAPHL	PAPHM	PAPHN	PAPHE
Geological				
DZLIMEST	b	b	.38±.26	.36±.10
PAPHSOIL	3.9±.9	2.4±.8	1.85±.6	b
CONTDUST	b	b	b	1.5±.2
Secondary				
SULFATE	7.4±1.2	c	b	7.2±1.1
NITRATE	c	c	c	c
Other				
PBAUTOEX	3.4±.5	3.0±.5	2.8±.4	2.5±.5
RESIDOIL	.36±.10	.36±.10	.36±.09	.18±.06
ALUMPROC	b	b	b	b
ZOLLERCU	.52±.39	3.0±2.3	1.2±.9	.52±.38
VEGBURN2	b	b	4.5±2.0	1.1±.5
VEGBURN1	4.1±1.3	18.9±3.3	b	c
PAPHMN	.15±.14	b	b	c
Total:	19.9±2.1	27.7±4.1	11.1±2.3	13.4±1.4
Percent of Measured Mass:	67±11%	85±15%	38±9%	64±8%

AVERAGE COARSE SOURCE CONTRIBUTIONS (ug/m^3)

Source Type	Sampling Site PAPHL	PAPHM	PAPHN	PAPHE
Geological				
DZLIMEST	2.1±.4	3.1±1.0	1.9±.3	1.3±.2
DZCRUSTA	6.9±.8	12.8±1.0	9.1±.8	5.9±.5
Secondary				
SULFATE	c	c	c	c
NITRATE	c	c	c	c
Other				
PBAUTOEX	1.1±.2	.77±.18	.61±.14	.59±.13
MARINE	.83±.31	.75±.25	.72±.23	.51±.30
ZOLLERCU	.46±.35	2.5±.5	2.2±.4	1.0±.4
ALUMPROC	2.4±.6	4.6±.9	3.2±.6	2.4±.5
PAPHMN	5.9±1.6	.16±.05	.09±.03	.06±.02
Total:	19.7±2	24.8±1.8	17.9±1.1	11.8±.9
Percent of Measured Mass:	95±17%	108±11%	83±14%	111±12%

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[b] Not needed to fit.
[c] Not included due to lack of data.

These conclusions justify the use of one sampler on the perimeter of the Bridesburg area to represent average mass concentrations of FP and IP, but they do not justify the use of a single sampler to identify and quantify the sources of CP, and therefore of IP. Apparently, relative source contributions to IP vary from sampling site to sampling site even though the sum of those contributions may be the same. Thus, detailed receptor-oriented source apportionment on the industrial neighborhood-scale may require a number of sampling sites. This condition may be less stringent on the urban-scale or on the non-industrial neighborhood-scale. These observations are, of course, to be considered with their limitations outlined in Section 9.3.

This chapter has attempted to identify and quantify the sources of FP, CP and IP using receptor-oriented models. The limitations of these models applied to the present situation are evident and have been pointed out. Nevertheless, these efforts have resulted in some observations about the chemical concentrations from receptor samples in the IP Network data base and the possible contributors to those concentrations.

- Data validation procedures should be applied to IP Network chemical concentrations to identify and remove suspicious values which can bias the results of receptor model source contribution estimates.
- The identification of likely contributors due to the close geographical proximity of a major source to a receptor is often confirmed by chemical concentration measurements and receptor model source contribution estimates.
- The chemical element balance and microscopic properties balance receptor models exhibit major limitations. Despite these limitations, it appears that major contributors to IP Network sites in the eastern United States are unaccounted for sulfate (possibly from the conversion of SO_2) and motor vehicle exhaust in the average FP fraction and geological material and possibly biological material in the average CP fraction. Industrial point sources show small (less than 1 ug/m^3) contributions to both size fractions at urban-scale sites in most cases. Data are insufficient to apply these observations to western sites.

- In an industrial neighborhood, one sampling site may be able to measure average IP mass concentrations equivalent to those at a nearby site, but the sources contributing to those concentrations may be different. A receptor model approach to quantifying source contributions in such neighborhoods may require more than one sampling site.

CHAPTER 10

SUMMARY, CONCLUSIONS AND FUTURE RESEARCH

This study of measurements acquired during the first year of monitoring of the EPA's IP Network has answered some questions and raised others. It is appropriate here to summarize the contents of this report, to determine the extent to which questions have been answered, to outline further work which will be required to confirm those answers and to address those issues that remain to be explored.

The underlying message of this work is that the interpretation of environmental measurements for descriptive, cause-effect, and policy formulation considerations cannot be separated from the measurement process. Thus, this report has combined at every step assessments of the effects of measurements on conclusions. This summary must include the conclusions and recommendations about the measurement process as well as conclusions about total, inhalable and fine suspended particulate matter concentrations in the United States.

Chapter 1 set the stage by proposing a list of questions concerning inhalable particulate matter which might or might not be answered through the analysis of IP Network measurements and information obtained in other studies. A technical approach involving literature review, hypothesis forming and hypothesis testing using IP Network measurements was outlined and was followed throughout the study.

Chapter 2 dealt with the sampling devices used to acquire TSP, IP and FP samples. These included high-volume samplers, high-volume samplers with size-selective inlets, and dichotomous samplers. The collection effectiveness curves, which show the percent penetration of particles through a sampling inlet as a function of particle aerodynamic diameter, were drawn from a number of wind tunnel tests of samplers used in the IP Network. These curves were compared with an acceptable performance range which was proposed for 15 um cut-size inlets.

The collection efficiency, the fraction of the total aerosol mass collected by each sampler, was calculated by integrating the product of collection effectiveness and fractional aerosol mass concentration over all particle sizes. These efficiencies for different sampling devices under different wind speeds and particle size distributions were compared with each other. This treatment showed that, under wind speed and size distribution conditions typical of urban areas, the IP concentration should equal about 70% of the TSP concentration, TOTAL and SSI samples should not differ by more than 5%, and samples taken with a hypothetical 10 um cut-size inlet should sample 10 to 20% less mass than a 15 um cut-size inlet.

The Sulfate Regional Experiment (SURE) IP and FP collection characteristics were also examined. The IP fraction collected by this sampler was found to be approximately 10% smaller than that collected by the dichotomous sampler inlet while the FP collection efficiency was indistinguishable from the IP Network's FINE sample. This sampler was included so that SURE IP and FP data could be compared with IP Network data later in the report.

Only the SSI collection effectiveness fell within the proposed acceptable performance range though both the SSI and dichotomous samplers fell within the range of collection efficiencies corresponding the upper and lower limits of the acceptable performance range for typical wind speeds and size distributions.

A comparison of the ratios of collection efficiencies derived from the integration process with average ratios from ambient measurements showed a reasonable agreement, though the range of measured ratios was much larger than that predicted by the integration process. There was also some evidence that SSI mass measurements on certain samples consistently disagreed with simultaneous TOTAL measurements; an interference due to a change in filter media rather than changes in the inlet characteristics was suggested as a cause which merits further investigation.

Chapter 3 described the network, locating the areas sampled throughout the United States. When site surveys existed, the sources within the immediate environment of the sampler were noted. Each site was classified as being representative of an urban, suburban or rural area. The site survey information was found to be incomplete, and those sampling sites requring greater documentation were identified.

The significance of sulfate and nitrate artifacts was examined and these interferences were found to cause possible biases in mass, sulfate and nitrate measurements for a portion of the HIVOL and SSI samples. The fibrous filter medium used in HIVOL and HIVOL(SSI) samplers in the IP Network was changed from a quartz fiber filter used in 1979 to a glass fiber filter with organic binder used in 1980. Comparisons of average mass ratios of TOTAL/SSI showed 1.08 ± .23 in 1979 and .90 ± .21 in 1980. Similarly, the regression line slope of TOTAL vs. SSI sulfate measurements was 1.07 ± .07 for 1979 samples and .68 ± .05 for 1980 samples. A significant fraction of the difference between SSI and TOTAL mass measurements could be accounted for by artifact formation on samples taken after the beginning of 1980.

The measurement methods followed to obtain the data in the IP data base were briefly described. Standard operating procedures summaries for filter weighing, ambient sampling, and chemical analyses for ions, elements, carbon and microscopic analyses were presented.

The descriptions were brief and were intended to be pointers to the more detailed procedures. It was observed that complete characterization of the methods and procedures was not available to this study due to the youth of the IP Network, but that such a characterization would be necessary by the time IP Network sampling is completed.

The data validation process through which all IP Network measurements passed is probably the most comprehensive of any of EPA's large-scale monitoring networks. It involved timing, duration, flow rate, calibration, and visual inspection checks in the field. Re-weights were performed in the laboratory. Transcription, outlier and internal consistency checks were made at data processing. Still, inconsistencies in individual data values were common, and though these had been flagged in most cases by the routine validation procedures, an additional screening based on reasonable limits suggested by typical ambient particle size distributions was followed to eliminate the most blatant inconsistencies. Later in the study a similar, but more subjective, screening was applied to chemical concentration measurements. In the cases of the seasonal averages at urban and background sites, this screening procedure was not followed and the summary statistics were used exactly as they came from EPA. Where differences are detected between the results of analyses presented here and similar analyses by other researchers using the same data, they are most likely due to this additional validation process.

The final section of Chapter 3 evaluated the accuracy and precision of the mass measurements obtained by IP Network sampling equipment. The effects of recirculation of HIVOL copper and carbon emissions were examined, and studies were cited which showed that these contributions to mass and carbon concentrations were negligible, but that HIVOL and SSI copper measurements could be biased. Comparisons of simultaneous TOTAL and SSI copper measurements lent credence to this proposition.

The effects of passive deposition on HIVOL filters over the 6-day period between samples was examined via a review of several studies which consistently showed an average bias of +10 to +15% with up to +25% increases in TSP for individual samples under certain conditions. Removal of particulate matter from filters during passive sampling was found to be negligible. No reports of such passive sampling tests on HIVOL(SSI) and dichotomous samplers were found.

Collocated sampling results indicated precisions of ±5% for HIVOL and SSI mass measurements, ±7% for FINE measurements, and ±10% for TOTAL and COARSE measurements greater than 10 ug/m^3. These precisions must be considered those attainable by IP Network sampling and not necessarily the precisions to be associated with any particular set of values.

In Chapter 4, the characteristics of the urban areas containing IP sampling sites were summarized. Long-term average meteorological information and current demographic and geographic descriptions were given.

Seven urban areas were selected for more detailed examination: Birmingham, AL, Buffalo, NY, Denver, CO, Phoenix, AZ, Houston, TX, El Paso, TX, and Philadelphia, PA. Point sources of TSP emissions were identified and placed on maps in relation to the receptor sites. The source types identified were tabulated and assigned dominant chemical components and particle sizes on the basis of literature review. Speculations were made concerning the expected ambient concentrations, speculations which were tested in Chapter 9. In particular, a lead smelter was expected to have a major influence on concentrations in El Paso, TX, the iron and steel industry was expected to influence samples in Buffalo, NY, and a number of closely spaced industries was expected to affect neighborhood-scale sampling sites in an industrial area of Philadelphia.

Chapter 5 undertook the task of presenting the spatial and seasonal variation of TSP, IP, and FP concentrations in urban areas with an eye to determining which areas of the United States would be most likely to exceed a standard, what the causes of elevated and depressed concentrations might be, the necessary sampler spacing required to represent different neighborhoods and the sampling schedule required to estimate an annual mean. Los Angeles, Birmingham, and El Paso showed the highest IP concentrations based on IP Network data. Urban FP concentrations in the West were generally lower than those in the East, though the paucity of western sites with sufficient data limits the validity of this conclusion.

Several sampling sites seem to be required to characterize IP and FP concentrations in a single urban area. In a highly industrialized neighborhood, major differences in TSP and IP concentrations were found between sites spaced only one or two kilometers from each other even though these mass concentrations were similar to those at other nearby samplers. Significant seasonal variability of averages and maxima did not manifest itself at all sites, but it was observed at enough sites to conclude that year-long sampling is required to achieve an unbiased average.

The spatial and seasonal variability of non-urban TSP, IP and FP concentrations was dealt with in Chapter 6. Non-urban IP average concentrations were found to be more or less comparable in the eastern and western United States though the distribution between fine and coarse particles was different. It was speculated that the higher FP component in the East was due to a greater preponderance of sulfate and that the larger CP component in the West was due to greater quantities of suspended geological material. This observation was tempered by the small number of western sites reporting data. No marked seasonal variations were noted in western IP and FP concentrations, but these concentrations did increase during the summer months in the eastern United States.

When comparing non-urban to urban concentrations it was concluded that about 50% of the TSP, 60% of the IP and 70% of the FP found in urban areas could be due to origins outside of those areas. These percentages are upper limits due to the likelihood that a portion of the non-urban concentrations is derived from local, non-urban sources.

The frequency distributions of mass concentrations were studied in Chapter 7; the log-normal model was chosen as the most appropriate one for representing ambient suspended particulate matter measurements, and HIVOL and SSI measurements seemed to fit this model fairly well. TOTAL, FINE, and COARSE concentrations for the whole network showed a significant deviation from the distribution. The 99th percentile concentrations of all measurements acquired in the network were 210, 170, 150, 80 and 90 ug/m^3 for HIVOL, SSI, TOTAL, FINE, and COARSE mass concentrations, respectively.

The use of an arithmetic over a geometric average was addressed. From a practical standpoint it was found that the two averages vary by only about 10% and that the variability is fairly independent of sample size. Thus, it seems that either one could be used for long-term standards.

The variability of the arithmetic average and 24-hr maximum concentrations as a function of sampling frequency was studied by re-estimating them using data sets from which every other record had been removed. Sampling intervals of up to 24-day were possible before major differences in the calculated averages appeared. Maximum concentrations were found to be highly dependent on sampling intervals.

The average ratio of IP/TSP was examined in Chapter 8 as a function of site classification and TSP concentration. Different relationships were found for SSI/HIVOL, $.72\pm.13$ irrespective of HIVOL concentration, and for TOTAL/HIVOL, $.75\pm.18$ for TSP less than 100 ug/m^3, and $.63\pm.16$ for TSP greater than 100 ug/m^3.

The utility of using these ratios to predict IP concentrations from TSP measurements was examined and for all IP Network data they predicted SSI concentrations within ±30% in 89 out of 100 cases and

TOTAL concentrations within ±30% in 80 out of 100 cases. The prediction error was found comparable to the error of estimating the concentration at a location from an IP measurement at a nearby site. No consistent relationship was found between FP and TSP concentrations.

In Chapter 9, the spatial distributions of chemical species concentrations in the Buffalo, Houston, El Paso and Philadelphia areas were examined to address the speculations of Chapter 4. In general, the chemical species measurements confirmed those speculations. Urban sites showed enrichments over background sites, and receptors closer to industrial sources with unique chemical emissions exhibited higher concentrations of these species in certain cases.

The chemical element balance receptor model using two original source samples from Philadelphia and others from previous studies was applied to average chemical concentrations at urban-scale and neighborhood-scale sites. This model and the microscopic properites balance model were also applied to a selected number of individual samples. The conclusions concerning results derived from these models are especially guarded since the major efforts required to overcome their limitations were not undertaken as part of this study. Nevertheless, it appears that in urban areas of the eastern United States, the major contributor to the FP fraction is sulfate which cannot be accounted for by other sources and is possibly of secondary origin. The next largest general contributor is automobile exhaust. From 25% to 50% of the FP mass is often unaccounted for, however, which may be due to chemical species, such as ammonium and carbon, which are not measured in the IP Network. On CP samples, geological material seems to dominate and 100% of the mass is normally accounted for, though there is a discrepancy between the chemical and microscopic evaluations of the sources contributing to this size fraction.

A set of questions was proposed in Chapter 1 which the IP Network was intended to answer. After this review of the data acquired in that network, it is possible to evaluate the extent to which the network has answered these questions.

With regard to the sources of IP, the question of probable sources has been answered by the compilation of emissions inventories and the examination of the chemical concentrations. Several important chemical components are missing, however, notably ammonium, sodium, elemental carbon, organic carbon and vanadium, which would aid in the quantification of sources. Aerosol formed from the conversion of gases, fugitive dust, and motor vehicle exhaust all seem to be important contributors in the eastern United States while ducted, industrial emissions appear to be minor contributors. The data from the western United States were insufficient to answer the questions.

In relation to mass, chemical and size characterization, it appears that differences between these characteristics are not generally related to site-type classification with the exception of urban vs. non-urban categories. This may be due to the subjective manner in which classifications are assigned. The ratio of IP to TSP is variable and does not appear to depend on the site type. Though theoretical studies show that IP measurements made with HIVOL size-selective inlets and dichotomous samplers should be equivalent, simultaneous sampling shows that they differ; this may be due to the adsorption of gases on the SSI filters. The ratio of IP to TSP varies because of sampling as well as ambient changes which include wind speed, size distribution and filter media. The ranges and averages of mass concentrations in different areas are obtainable from IP Network data, but they depend upon the number of samples obtained and the frequency of sampling.

The spatial distributions of IP and FP concentrations show that FP mass concentrations are fairly uniformly distributed across urban areas, with some notable exceptions, while IP mass concentrations are not. Gradients are significant with respect to instrument siting and control strategy development; even though the average mass concentrations at neaby sites may be nearly the same, the sources contributing to those concentrations may not be the same. The scale of representativeness of IP monitors is very specific to the area under study and only warnings, not generalizations, can be drawn from IP data. IP Network data is insufficient to determine the vertical distribution of concentrations near sources.

The IP Network sampling schedule does not permit diurnal or weekday/weekend variability to be evaluated. Changes in seasonal averages of mass and chemical concentrations can be discerned, but the data available for this report was too limited to form generalizations. When more than two years of data become available these observations can be made.

The number of regional-scale sampling sites in the IP Network with sufficient data was too small to form major conclusions concerning the transport, transformation and background concentrations. Associated meteorological measurements and short-term, multi-day samples required to characterize the events associated with long-range transport are also lacking. Other networks do provide IP and FP data, e.g., the SURE/ERAQS network in the eastern United States (Mueller and Hidy et al, 1981) and the WRAQS (Hilst, 1981) and VIEW (Cahill et al, 1981) networks in the western United States which meet these requirements.

Some of the SURE data was used in this report, but not to the extent necessary to answer the questions in Table 1.1. The unification of the IP Network and other, related data sets could provide a cost-effective extension of IP Network measurements.

The text of this report is laced with recommendations about the measurement process and the need for further data interpretation. There is no doubt that the wealth of information in the IP Network data base has barely been tapped. With some reasonable changes in operating and reporting procedures this wealth could be enhanced.

Since a "tentative" label has been applied to most of the observations in this report due to the limited quantity of measurements available to it, the major recommendation is that the treatments of Chapters 5 to 9 should be applied to a more extensive data set, presumably the one which will be available in the IP Network after this report is published. Since attention is shifting from inhalable particulate matter in the 0 to 10 um range in place of the 0 to 15 um range, data from networks acquiring measurements in this new size range should be submitted to the interpretative efforts of this report and others as soon as they are available. These further data analyses could benefit from the following suggestions:

- The equivalence of wind tunnel tests should be established, and the Beckman and Sierra inlets should be tested under similar conditions to evaluate their equivalence.

- A complete evaluation of the glass fiber filter media needs to be made and, if possible, one should be used which will not exhibit artifact formation.

- Site surveys should be completed for all sites and a meaningful site classification scheme should be devised and applied.

- Data validation procedures should be devised and used to reject certain values when calculating summary statistics. These need to be applied to chemical components as well as to mass measurements. Precision and accuracy results should accompany measurements. These should be specific to each measurement and not applied to the IP Network as a whole.

- Vanadium and chromium concentrations obtained from x-ray fluorescence should be included in data reports. Consideration should be given to non-routine but regular sodium, ammonium, carbon and microscopic analyses of samples.

- Emissions inventories in each urban area sampled by the IP Network should be reduced to locations with respect to sampling sites, and source compositions for similar sources should be assembled. Initial receptor modeling should be performed and appropriate samples should be taken of the source types they identify for more refined modeling.

- Spatial and seasonal averages of IP and FP for multiple years should be examined to confirm whether or not they repeat themselves.

- The measurement processes of data from other networks which might supplement IP Network data should be evaluated so that interpretation of that data can be properly carried out.

- Patterns in log-normal frequency distributions of IP and CP similar to those found for TSP should be sought at individual sites. Forms of a standard other than annual average and maximum concentration should be formed and the effects of frequency, location and method of sampling on their attainment should be evaluated.

- Additional models for predicting IP and FP concentrations from TSP should be devised and tested.

- The present and additional receptor models should be tested in greater detail according to a predefined protocol to determine their applicability to IP Network data.

In general, the IP Network has accomplished its goals of providing a data base from which certain observations can be made and hypotheses can be formed. The data included in this report, however, are too limited to draw definitive conclusions. Many of the interpretative efforts made here should be applied again when the data base is more complete.

APPENDIX A
SAMPLING SITE DESCRIPTIONS

TABLE A.1 SAMPLING SITES IN THE IP NETWORK

SITE CODE	SITE DESCRIPTION & SITE ADDRESS	A	B	C	ELEVA -TION (FT.)	SAROAD	UTM X	UTM Y	PROBE HT. (METER)	START DATE	END DATE	E	F	G
ALBIA12	S. BIRMINGHAM 720 20TH ST. BIRMINGHAM,AL	1	0	0	---	010380003	518.630	3707.064	11	79/07/14	80/06/14	1	0	1
ALBIB23	INGLENOOK 3937 44TH AVE. BIRMINGHAM,AL	0	0	0	---	010380026	520.627	3713.626	--	79/07/20	80/06/14	1	0	1
ALBIC21	N.BIRMINGHAM 3009 28TH ST. BIRMINGHAM,AL	0	*	1	600.	010380023	517.300	3712.420	--	79/07/08	80/06/14	1	1	1
ALBID23	MOUNTAIN BROOK 3015 OVERTON ROAD, BIRMINGHAM,AL	1	0	0	---	012540001	524.100	3703.000	03	79/08/01	80/06/14	1	0	1
ALBIE21	TARRANT CITY 1818 PINSON ST. BIRMINGHAM, AL	1	0	0	---	013200001	521.500	3715.900	05	79/07/26	80/06/14	1	1	1
AZANA007	APACHE NATIONAL FOREST NFOS WATERSHED, AZ	0	0	0	---	030380110	-------	--------	--	80/05/09	80/06/14	1	0	0
AZPHA357	CAREFREE AIRPORT, PHOENIX, AZ	0	1	0	---	030440006	416.964	3742.146	--	79/09/06	80/05/15	1	0	1
AZPHB13	MARICOPA CO. HEALTH DEPARTMENT 1845 ROOSEVELT ST. PHOENIX, AZ	0	*	1	1135.	030600002	403.195	3702.388	11	79/08/31	80/03/28	1	0	0
AZPHC23	NORTH PHOENIX 8531 N. 6TH ST. PHOENIX, AZ	0	1	0	---	030600004	401.263	3712.940	--	79/08/13	80/05/15	1	1	1
CAFPA34	UNIVERSITY OF CALIFORNIA CA U. EXP. STATION, FIVE POINTS, CA	0	0	0	---	052820002	759.855	4025.499	--	79/09/30	80/06/14	1	1	1
CALAA237	AZUSA 803 N. LOREN AVE, LOS ANGELAS, CA	0	1	2	615.	050500002	414.892	3777.371	05	79/08/13	80/06/14	1	1	1
CALAB227	W. L. A. 1535 S. ROBERTSON BLVD. LOS ANGELES, CA	0	1	1	---	054180103	-------	--------	06	79/07/08	80/06/14	1	1	1
CALAC23	PASADENA 1196 E. WALNUT ST. LOS ANGELES, CA	0	1	2	838.	055760004	396.420	3779.120	06	79/07/20	80/06/14	1	1	1
CALAD237	RUBIDOUX (METROPOLITAIN L. A.) 5888 MISSION BLVD. LOS ANGELES, CA	0	1	2	820.	056535001	462.161	3757.641	07	79/08/25	80/06/20	1	1	1
CASFA23	LIVERMORE 2131 RAILROAD AVE. SAN JOSE, CA	0	1	1	---	054020002	608.533	4171.121	08	79/09/24	80/05/09	1	0	1
CASFB22	RICHMOND 1149 13TH ST. SAN FRANCISCO, CA	0	1	2	2.	056300003	556.620	4194.572	09	79/09/24	80/06/14	1	1	1
CASFC007	SAN FRANCISCO EAST 900 23RD ST. SAN FRANCISCO, CA	0	1	1	---	056860003	551.439	4176.209	09	79/11/16	80/05/03	1	0	1
CASJA12	UNIVERSITY 120 N. 4TH ST. SAN JOSE, CA	0	1	2	108.	056980004	598.400	4133.000	04	79/09/30	80/06/20	1	0	1
CODFA12	DOWNTOWN 414 14TH ST. DENVER, CO	0	1	2	5656.	060580001	500.691	4398.839	14	00/00/00	00/00/00	1	1	0

TABLE A.1 (CONTINUED)

SITE CODE	SITE DESCRIPTION & SITE ADDRESS	A	B	C	ELEVA -TION (FT.)	SAROAD	UTM X	UTM Y	PROBE HT. (METER)	START DATE	END DATE	E	F	G
CODEB11	GATES RUBBER COMPANY 1050 S. BROADWAY, DENVER, CO	0	1	2	5288.	060580003	501.187	4394,072	11	00/00/00	00/00/00	0	0	0
CTHFA12	PUBLIC LIBRARY MAIN ST. HARTFORD, CT	0	*	2	40.	070420003	693.300	4625,800	12	80/02/03	80/05/27	1	1	1
CTHFB35	LITCHFIELD COUNTY MORRIS DAM, RT. 109, HARTFORD, CT	0	0	0	---	070478001	654.580	4614.900	--	79/12/11	80/01/16	1	0	1
DCDCA12	DOWNTOWN 24TH & L ST. NW, WASHINGTON D C	0	*	1	66.	090020017	322,095	4307,905	10	79/09/06	80/05/27	1	0	1
DEDOA12	DOVER POLICE STATION DOVER, DE	0	0	0	---	080020001	456,793	4333,175	--	79/08/31	80/05/09	1	0	1
GEATA12	FULTON CO. HEALTH DEPT. 99 BUTLER ST. SE, ATLANTA, GE	0	0	0	600.	110200001	-------	--------	06	00/00/00	00/00/00	0	0	0
HIHOA23?	LEEWARDS MEDICAL CENTER 860 FOURTH ST. PEARL C, HONOLULU,HI	0	*	1	80.	120370004	618,446	2356,940	--	79/09/30	80/05/27	1	1	1
IAMAA00?	CENTER CITY 24 N. CENTER ST. MARSHALL TOWN, IW	0	0	0	---	162500003	-------	--------	--	00/00/00	00/00/00	0	0	0
IAMAB00?	FISHER SCHOOL 2001 S 4TH ST. MARSHALL TOWN, IW	0	0	0	---	162500004	-------	--------	--	00/00/00	00/00/00	0	0	0
ILBRA34	SEWAGE TREATMENT PLANT BRAIDWOOD, IL	0	0	0	---	148320007	397.802	4570,111	--	79/09/18	80/06/02	1	0	1
ILCHA13	FARR DORM 3300 S. MICHIGAN AVE. CHICAGO, IL	0	*	2	636.	141220014	444.149	4636,088	--	79/10/30	79/12/11	1	0	0
ILCHB11	WASHINGTON HIGH SCHOOL 3500 E. 114TH ST. CHICAGO, IL	0	*	2	616.	141220022	455.030	4615.074	--	00/00/00	00/00/00	0	0	0
ILCHC00?	RIVER FOREST JR. HIGH SCHOOL OAK & LATHROP ST. CHICAGO, IL	0	0	0	---	146540001	432,456	4637.969	--	79/09/30	79/09/30	1	0	0
KSKAA11	FAIRFAX FIRE STATION 3105 FAIRFAX RD. KANSAS CITY, KS	1	1	1	700.	171800011	360.841	4332,598	03	80/02/03	80/06/08	1	0	1
LAKIA11	CATAHAULA WORK CENTER KISATCHIE NAT'L FOREST, POLLOCK, LA	0	0	0	---	191490101	550,121	3484,951	--	79/10/11	80/04/27	0	0	1
MABOA12	115 EAST BOSTON SOCIAL CENTER 68 CENTRAL SQUARE, BOSTON, MA	0	0	0	---	220240013	331,903	4693,212	--	79/12/11	80/05/15	1	0	1
MABOB12?	BOSTON FIRE HEADQUATER 115 E. HAMPTON ST. BOSTON, MA	0	*	2	25.	220240012	329.580	4688,230	--	79/12/05	80/05/15	1	1	1
MDBAA22?	S.E.POLICE STATION 5700 EASTERN AVE. BALTIMORE, MD	0	0	0	---	210120008	366.490	4349,610	--	00/00/00	00/00/00	0	0	0
MDBAB23	S.W.POLICE STATION 434 S. FONTHILL AVE. BALTIMORE, MD	0	*	1	105.	210120009	356.479	4348.709	06	79/08/31	80/03/10	1	0	1
MDDUA23	SOLLERS POINT CENTER SOLLAR ST. DUNDALK, MD	0	0	0	---	210620001	369.715	4344.742	--	79/08/31	79/08/31	1	0	0

TABLE A.1 (CONTINUED)

SITE CODE	SITE DESCRIPTION & SITE ADDRESS	A	B	C	ELEVA -TION (FT.)	SAROAD	UTM X	UTM Y	PROBE HT. (METER)	START DATE	END DATE	E	F	G
MEACA35	ACADIA NATIONAL PARK MCFARLAND HILL,U233, BAR HARBOR, ME	0	0	0	---	200010001	555,380	4898,460	--	00/00/00	00/00/00	0	0	0
MIDEA11	S.W.HIGH SCHOOL 6601 W. FORT, DETROIT, MI	0	*	2	1000.	231180015	326,312	4685,539	04	00/00/00	00/00/00	0	0	0
MIDEB12	AIR POLLUTION CONTROL HQ. 1311 E. JEFFERSON AVE, DETROIT, MI	0	*	2	600.	231180020	332,450	4688,700	07	00/00/00	00/00/00	0	0	0
MOMTA00	MARK TWAIN NATIONAL FOREST MARK TWAIN NATIONAL FOREST,MO	0	0	0	---	262950001	-------	--------	--	79/05/21	80/06/18	1	0	0
MNMIA13	REGINA HIGH SCHOOL 4255 3RD AVE. MINNEAPOLIS, MN	0	*	2	855.	242260049	478,450	4965.372	05	79/09/24	80/06/20	1	0	1
MNMIB12	DOWNTOWN 300 NICOLLET MALL, MINNEAPOLIS, MN	0	0	0	---	242260051	478,750	4980,600	--	79/11/05	80/06/14	1	0	1
MOKAA12	FIRE STATION 1517 LOCUST ST. KANSAS CITY, MO	0	*	0	---	262380002	363,579	4328,351	--	80/02/09	80/06/08	1	1	1
MOSLA22	TRAILER 5962 LINDBURSH AV. ST. LOUIS, MO	0	1	1	600.	260030001	731,500	4266,800	03	80/01/28	80/06/20	1	0	1
MOSLB13	FIRE STATION BROADWAY & HURCK. ST. LOUIS, MO	1	*	1	500.	264280007	738,493	4269.352	10	00/00/00	00/00/00	0	0	0
MTASA35	CUSTER NATIONAL PARK FT. HOWES RANGER STATION, DISTRICT #5, ASHLAND,MT	0	0	0	---	270310101	401,878	5009,413	--	00/00/00	00/00/00	0	0	0
NCCNA00	CROATAN NATIONAL FOREST 435 THURMAN RD, NEW BERN, NC	0	0	0	---	340945101	-------	--------	--	80/04/15	80/06/08	1	0	0
NCDUA11	CAMEO BUILDING S. MANGUM ST. DURHAM, NC	0	0	0	---	341160006	689,150	3985.106	--	80/05/03	80/05/15	1	1	0
NCDUB007	DURHAM DURHAM, NORTH CAROLINA	0	0	0	---	341160101	689,677	3985,025	--	80/07/26	80/05/27	1	1	1
NCREA327	BEAUNIT BUILDING ALEXANDER DR. ERC ANNEX, RTP, NC	0	0	0	---	341160001	-------	--------	--	00/00/00	00/00/00	0	0	0
NJLIA23	ST. BARNABAS HOSPITAL OLD SHORTHILLS RD. LIVINGSTON, NJ	0	0	0	---	311380001	558,800	4512,600	--	00/00/00	00/00/00	0	0	0
NJLAA34	LAKEHURST OFF HWY 527-528, VAN HISEVILLE, NJ	0	0	0	---	313900005	559,000	4439,500	--	79/08/09	79/09/05	1	0	1
NVWIA34	WINNEMUCCA 25 W. 4TH ST. WINNEMUCCA, NV	0	0	0	---	290580002	438,000	4536,000	--	79/09/30	80/05/27	1	0	1
NYBKA11	GREEN POINT POLLUTION CONTROL PL 301 GREEN POINT AVE. BROOKLYN, NY	0	*	1	30.	334680011	588,899	4509,415	06	00/00/00	00/00/00	0	0	0

TABLE A.1 (CONTINUED)

SITE CODE	SITE DESCRIPTION & SITE ADDRESS	A	B	C	ELVEA -TION (FT.)	SAROAD	UTM X	UTM Y	PROBE HT. (METER)	START DATE	END DATE	E	F	G
NYBRA13	P.SCHOOL NO. 111 BAYCHESTER AVE. BRONX, NY	0	0	0	---	334680068	597.648	4525.531	--	00/00/00	00/00/00	0	0	0
NYBUA11	P.SCHOOL NO. 26 84 HARRISON ST, BUFFALO, NY	0	1	1	0.	330660003	677.600	4748.400	06	79/08/25	80/06/20	1	0	1
NYBUB23	BIG SISTER SEWAGE TREATMENT PLT OLD LAKE SHORE RD. ANGOLA, NY	0	1	1	---	332000003	670.000	4722.280	02	79/08/25	80/06/20	1	0	1
NYBUC11	P.SCHOOL NO. 28 1515 S. PARK AVE. BUFFALO, NY	0	1	0	---	330660010	677.800	4746.900	08	79/08/25	80/06/20	1	0	1
NYBUD11	WILMUTH PUMP STATION WILMUTH AVE. BUFFALO, NY	0	1	0	---	333520001	676.600	4743.100	02	79/09/18	80/06/20	1	1	1
NYMAA13	MARBLE DEAN BACON HIGH SCHOOL 240 2ND AVE. MANHATTEN, NY	0	*	1	125.	334680010	585.607	4510.116	24	00/00/00	00/00/00	0	0	0
OHAKA11	JOHN D. MORLEY HEALTH BUILDING 177 S. BROADWAY, AKRON, OH	0	0	0	---	360060014	456.563	4547.563	--	79/06/08	80/06/20	1	1	1
OHCIA23	DRAKE HOSPITAL GALBRAITH RD. CINCINNATI, OH	0	0	0	---	361220020	717.400	4343.000	--	79/08/07	80/06/20	1	1	1
OHCLA11	AIR POLLUTION CONTROL DIV. HQ. 2785 BROADWAY, CLEVELAND,OH	0	0	0	---	361300013	443.800	4592.400	--	79/07/26	80/02/09	1	1	1
OHCLB13?	J.F. RHODES HIGH SCHOOL BIDDULPH & W. 54TH ST, CLEVELAND, OH	0	*	2	812.	361300021	439.700	4586.600	15	80/02/03	80/03/16	1	0	1
OHCLC13	WASHINGTON PARK HORT. SCHOOL 3875 WASHINGTON PARK BLVD. CLEVELAND, OH	0	0	0	---	361300041	444.800	4589.200	--	80/02/09	80/03/16	1	1	0
OHMEA23	MEDINA VOCATIONAL SCHOOL 1101 WEST LIBERTY, MEDINA, OH	0	0	0	---	364140002	424.162	4556.124	--	80/01/22	80/06/08	1	1	1
OHMIA23	ARMCO-WILSON SCHOOL MIDDLETOWN, OH	0	0	0	---	364340005	724.205	4372.375	--	80/03/13	80/05/21	1	1	0
OHMIB23	ARMCO RESEARCH MIDDLETOWN, OH	0	0	0	---	364340006	724.205	4372.375	--	80/03/13	80/06/11	1	1	1
OHMIC21	ARMCO YANKEE GATE MIDDLETOWN, OH	0	0	0	---	364340007	724.205	4372.375	--	80/03/13	80/06/11	1	1	1
OHMID21	QUEIDA ARMCO MIDDLETOWN, OH	0	0	0	---	364340008	724.205	4372.375	--	80/03/13	80/05/21	0	1	0
OHMII007	ARMCO COKE PLANT GATE MIDDLETOWN,OH	0	0	0	---	364340009	724.205	4372.375	--	80/03/13	80/05/21	1	1	0
OHMIL007	ARMCO COKE PLANT GATE MIDDLETOWN,OH (COLLACATED)	0	0	0	---	364340009	724.205	4372.375	--	80/03/13	80/05/21	1	1	0
OHSTA13	WASHINGTON SCHOOL 814 ADAMS ST. STEUBENVILLE, OH	0	0	0	---	366420012	532.000	4467.500	--	79/05/21	80/05/21	1	1	1
ORPOA34	SAUVEE ISLAND GAME COMMISSION GAME COMMISSION, PORTLAND, OR	1	0	0	---	380500104	-------	--------	04	79/09/24	80/06/08	1	1	1

TABLE A.1 (CONTINUED)

SITE CODE	SITE DESCRIPTION & SITE ADDRESS	A	B	C	ELVEA -TION (FT.)	SAROAD	UTM X	UTM Y	PROBE HT. (METER)	START DATE	END DATE	E	F	G
ORPOB12	CENTRAL FIRE STATION 55 SW.ASH ST. PORTLAND, OR	1	*	2	72.	381460015	525,826	5040,770	15	79/09/24	80/06/14	1	1	1
PADOA34	DOWINGTON 51 MARSHALLTON RD. DOWINGTON, PA	0	0	0	---	392460070	-------	--------	--	79/08/05	79/09/05	1	0	1
PAPHA12	500 S.BROAD BROAD & LOMBARD ST. PHILI, PA	1	*	1	70.	397140003	485,810	4421,350	12	79/04/24	80/06/08	1	1	1
PAPHB11	ALLEGHENY ALLEGHENY & DELAWARE AVE. PHILI, PA	1	1	0	---	397140019	491,670	4425,170	02	79/05/03	80/06/14	1	1	1
PAPHC23	BELMONT FILTER PLANT FORD RD. & MONUMENT RD. PHILI, PA	1	0	0	---	397140020	481,200	4427,820	02	79/06/08	79/10/06	1	0	1
PAPHD11	S.E. WATER TREATMENT PLANT FRONT ST. & PACKER AVE. PHILI, PA	1	*	1	23.	397140023	487,230	4417,330	01	79/06/14	79/09/30	1	1	1
PAPHE23	NORTH EAST AIRPORT GRANT AVE. & ASHTOWN RD. PHILI, PA	1	*	1	93.	397140024	498,970	4436,020	02	79/05/03	80/06/14	1	0	1
PAPHF12	H.GRATZ COLLEGE 10TH ST. & TABOR RD. PHILI, PA	0	0	0	---	397140032	61,296	4437,280	08	79/05/09	79/10/09	1	1	1
PAPHG13?	PRESBYTERIAN HOME 58TH ST. & GREENWAY AVE. PHILI, PA	0	0	0	---	397140036	480,066	4414,804	06	79/05/21	80/06/14	1	1	1
PAPHH12?	TEMPLE UNIVERSITY 12TH ST.& MONTGOMERY AVE. PHILI, PA	0	0	0	---	397140037	59,554	4433,219	06	79/05/15	79/09/30	1	0	1
PAPHI11?	ST.JOHN CATHOLIC CHURCH INTERSECTION OF ORTHODOX & ALMOND ST. PHILI, PA	0	1	0	---	397140038	493,600	4427,500	02	79/05/27	80/06/14	1	1	1
PAPHJ11	PILOT FREIGHT COMPANY 2840 HEDLEY & BATH ST. PHILI, PA	0	1	0	---	397140040	493,600	4426,900	02	79/10/15	80/02/19	1	1	1
PAPHK11	N.E. WASTEWATER TREATMENT PLANT FRONT ST. & PACKER AVE. PHILI, PA	0	1	0	---	397140041	492,600	4426,100	03	79/10/09	80/02/15	1	1	1
PAPHL11	T&A PET SHOP MERCER & W. MORELAND AVE. PHILI, PA	0	1	0	---	397140042	491,400	4426,000	02	79/10/21	80/02/15	1	0	1
PAPHM11	N.E. TRANSFER STATION 3901 N. DELAWARE AVE. PHILI, PA	0	1	0	---	397140043	493,200	4425,700	04	79/10/06	80/02/15	1	0	1
PAPHN11	BRIDESBURG RECREATION CENTER RICHMOND & BUCKIUS ST. PHILI, PA	0	1	0	---	397140044	494,200	4427,500	03	79/10/03	80/02/15	1	0	1
PAPHO11	500 S.BROAD (COLLOCATED SITE)	0	1	0	---	397140003	485,810	4421,3500	11	79/08/04	80/06/02	1	1	1
PAPIA23	IMPERIAL HIGH SCHOOL W ALLEGHENY HIGH SCH, PITTSBURG, PA	1	*	0	---	390100068	564,410	4476,777	05	79/08/19	80/05/03	1	0	1

TABLE A.1 (CONTINUED)

SITE CODE	SITE DESCRIPTION & SITE ADDRESS	A	B	C	ELEVA -TION (FT.)	SAROAD	UTM X	UTM Y	PROBE HT. (METER)	START DATE	END DATE	E	F	G
PAPIB23	NORTH BRADDOCK 600 ANDERSON ST. PITTSBURG, PA	0	0	1	900.	396620001	596.709	4472.824	04	79/08/13	79/11/05	1	0	0
PAPIC23?	HAZELWOOD NO.2 327 HAZELWOOD AVE. PITTSBURG, PA	0	*	1	920.	397260021	589.830	4473.980	04	79/08/13	80/04/09	1	0	1
TXDAA12	CONVENTION CENTER 727 AKARD ROAD, DALLAS, TX	0	*	2	450.	451310050	706.323	3628.147	--	80/01/16	80/06/14	1	1	1
TXELA12	TILLMAN TILLMAN HEALTH CENTER, EL PASO, TX	0	1	2	3762.	451700002	359.514	3514.263	07	79/11/23	80/06/14	1	1	1
TXELB34?	HIGH SCHOOL CLINT, TX	0	0	0	---	451700004	-------	--------	--	79/11/17	80/06/14	1	0	1
TXHOA23	ALDINE MAIL RD, CAMS 8 HAMBRICK JR. HIGH SCHOOL & MCARTHUR HIGH SCHOOL, HOUSTON, TX	0	1	2	50.	452330024	275.368	3307.063	--	79/12/05	80/04/15	1	0	1
TXHOB11	CAMS 1 1224 MAE DRIVE, HOUSTON, TX	0	1	2	45.	452560034	285.146	3295.380	02	79/11/23	80/05/15	1	1	1
TXHOC33	SEABROOK OFF RURAL RD.(SCH YARD),HOUSTON, TX	0	0	0	15.	454715001	304.643	3272.873	--	79/11/29	80/04/21	1	0	1
UTSAA23	MAGNA 2935 S. 8560 W. SALT LAKE CITY, UT	0	0	0	---	460520001	407.544	4506.431	--	00/00/00	00/00/00	0	0	0
UTSAB12	SALT LAKE CITY 610 S. 200 E. SALT LAKE CITY, UT	0	*	2	4250.	460920001	425.300	4511.800	--	00/00/00	00/00/00	0	0	0
VACUA34	CULPEPPER SR. HIGH SCHOOL RT. 229, CULPEPPER, VA	0	0	0	---	480880001	239.500	4264.800	--	00/00/00	00/00/00	0	0	0
WASEA21	DUWAMISH METRO-PUMP STATION 4500 E. MARGINAL WAY, S.SEATTLE, WA	0	*	1	14.	491840057	549.770	5267.740	11	00/00/00	00/00/00	0	0	0
WASEB23	SEATTLE CITY LIGHT COMPANY 98TH & STONE ST. SEATTLE, WA	0	*	1	310.	491840073	549.310	5283.000	04	79/09/30	80/06/20	1	0	1

COLUMN A : MICROINVENTORY
COLUMN B : LOCAL OR NAMS HARD COPY
COLUMN C : LOCAL OR NAMS SOFT COPY
COLUMN E : NUMBER OF HIVOL SAMPLER
COLUMN F : NUMBER OF HIVOL(SSI) SAMPLER
COLUMN G : NUMBER OF DICHOTOMOUS SAMPLER

APPENDIX B

AVERAGE METEOROLOGICAL MEASUREMENTS & URBAN CHARACTERISTICS OF IP NETWORK CITIES

TABLE B.1

AVERAGE METEOROLOGICAL MEASUREMENTS FOR IP NETWORK CITIES

Area	Normal Daily Mean Temp. Annual Avg. (°F)	Normal Daily Max. Temp. Annual Avg. (°F)	Normal Daily Min. Temp. Annual Avg. (°F)	Normal Precipitation Annual Avg. (in.)	Possible Sunshine Annual Avg. (%)	Windspeed Annual Avg. (mph)	7 a.m. & 1 p.m. Relative Humidity Annual Avg. (%)	Seasonal Heating Degree Days (65°F Base)	Snow & Ice Annual Avg. (in.)
Birmingham, AL	67.4	77.3	57.4	66.98	59	9.2	85 57	1,684	---
Phoenix, AZ	70.3	85.1	55.4	7.05	86	6.2	32 22	1,552	0
Los Angeles, CA	61.7	69.2	54.1	12.23	73	7.4	62 65	1,819	0
San Francisco, CA	56.9	65.1	48.7	19.53	67	10.5	69 62	3,042	0
Denver, CO	50.1	64.0	36.2	15.51	70	9.1	40 40	6,016	59.0
Hartford, CN	49.1	59.6	38.6	43.36	57	8.9	77 53	6,350	53.0
Washington, D.C.	57.3	66.7	47.8	38.89	58	9.3	73 52	4,211	16.3
Atlanta, GA	60.8	70.3	51.3	48.34	61	9.1	83 57	3,095	1.5
Honolulu, HA	76.6	83.3	69.8	22.90	67	11.8	70 56	0	---
Des Moine, IA	49.0	58.3	39.7	30.85	60	11.1	80 61	6,710	33.1
Chicago, IL	48.9	59.0	38.8	31.72	57	10.3	79 60	6,497	37.4
Boston, MA	51.3	58.7	43.8	42.52	60	12.6	72 58	5,621	42.1
Baltimore, MD	55.0	65.1	44.8	40.46	57	9.4	77 54	4,729	21.2
Detroit, MI	49.9	58.3	41.4	30.96	54	10.2	77 58	6,228	31.7
Minneapolis, MN.	44.1	53.8	34.3	25.94	58	10.5	79 60	8,159	46.1
Kansas City, MO	54.5	63.7	45.3	37.00	67	10.3	80 60	5,161	19.5
St. Louis MO	55.9	65.6	46.2	35.89	59	9.5	84 59	4,750	18.5
Raleigh-Durham, NC	59.1	70.4	47.8	42.54	60	7.9	84 54	3,514	6.8
Buffalo, NY	47.1	55.0	39.1	36.11	52	12.3	80 63	6,927	92.9
Cleveland/Akron, OH	49.7	58.5	40.8	34.99	52	10.8	79 63	6,154	52.2
Cincinnatti, OH	54.0	64.4	43.5	39.04	57	9.1	81 59	5,070	23.9
Portland, OR	52.6	61.6	43.6	37.61	48	7.8	72 60	4,792	7.4
Philadelphia, PA	54.6	64.2	44.9	39.93	58	9.6	76 55	4,865	20.2
Pittsburgh, PA	50.4	60.0	40.8	36.23	50	9.4	78 57	5,930	45.3
Dallas - Ft. Worth, TX	65.5	76.5	54.4	32.30	—	10.9	83 57	2,382	2.9
El Paso, TX	63.4	77.2	49.5	7.77	83	9.5	34 26	2,678	4.7
Houston, TX	68.9	79.8	58.0	48.19	57	7.6	91 60	1,434	0.4
Salt Lake City, UT	51.0	63.8	38.2	15.17	70	8.7	46 42	5,983	58.3
Richmond, VA	57.8	68.8	46.7	42.59	60	7.5	83 53	3,939	13.9
Seattle, WA	51.1	58.8	43.3	38.79	49	9.2	74 62	5.195	14.6

Source: Statistical abstract of U.S. 100th Ed. (1979). U.S. Dept. of Commerce
Bureau of Census

TABLE B.2

URBAN CHARACTERISTICS OF IP NETWORK CITIES

Area	Population Central City (1,000)	Population Metropolitan[a] Area (1,000)	Area Central City[a] (mi^2)	Area Metropolitan (mi^2)	Population Density Central City[b] People/mi^2	Major Industries[a]
Birmingham, AL	281	657	89	--	3,800	Steel and pipe manufacture
Phoenix, AZ	762	1,550	325	9,226	2,400	Electronic equipment and steel manufacture
Los Angeles, CA	2,800	10,900	464	--	6,100	Areospace industry, appliance, utility, and chemical manufacture
San Francisco, CA	642	--	45	--	15,800	Food, printing and fabricated metal products
Denver, CO	521	1,690	116	--	5,400	Rubber, luggage and furniture
Hartford, CN	--	--	--	--	9,100	--
Washington, D.C.	662	3,055	67	2,812	12,300	Government related activities, tourism
Atlanta, GA	456	1,907	136	4,326	3,800	Automotive assembly plant, airline and soda company
Honolulu, HA	729	912	595	--	3,900	Tourism
Des Monies, IA	201	338	66	--	3,200	Insurance center, tire center and auto accessories
Chicago, IL	2,900	7,049	228	4,657	15,100	Steel, metal products, food, paper and tool manufacturer
Boston, MA	637	2,899	46	--	13,900	Business, tourism and education
Baltimore, MD	821	2,164	91	2,225	11,600	Steel production, food, electronic and chemical products
Detroit, MI	1,258	4,386	140	--	11,000	Cars and trucks, metal and tool industry
Minneapolis, MN	350	1,233	59	4,000	7,900	Electronic computer manufacturer
Kansas City, MO	458	1,281	--	3,341	1,600	Stationary, farm equipment and frozen food products
St. Louis, MO	500	2,454	--	4,935	10,200	Auto and truck assembly plants
Raleigh-Durham, NC	175	515	51	--	2,700	Government related activities
Buffalo, NY	390	1,294	50	1,567	11,200	Iron and steel company
Cleveland, OH	609	1,939	--	1,519	9,900	Metal, steel, chemical and food products
Cincinnatti, OH	397	1,377	--	2,154	5,800	Jet engines, tools, chemicals, cosmetics and apparel manufacturer
Portland, OR	378	1,156	80	--	4,300	Electronic industries, lumber, wood and food products
Philadelphia, PA	1,800	4,800	130	3,553	15,200	Textile, apparel, food, petroleum and chemical manufacture
Pittsburgh, PA	422	2,277	56	--	9,400	Steel, coal, aluminum manufacture and nuclear power plants
Dallas-Fort Worth, TX	914	2,790	900	--	3,200	Oil field machinery, electronics, food and detergent producer, banking and insurance
El Paso, TX	448	--	239	--	2,700	Electronics, refinery and natural gas company
Houston, TX	1,700	2,900	556	--	2,800	Petrochemical and agriculture company and machinery manufacture
Salt Lake City, UT	180	868	--	--	3,000	Electronics, apparel manufacture and defense industries.
Richmond, VA	215	590	63	--	4,100	Tobacco and printing manufacture
Seattle, WA	498	1,527	92	--	6,400	Commercial jet aircraft, containerized shipping seaport, retail trade, transportation, wood and food products

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[a] Lane et al (1981), [b] U.S. Department of Commerce (1979)

APPENDIX C
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REFERENCES

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